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TECHNIQUES FOR THE ANALYSIS
OF COMPLEX SPECTRA
WITH APPLICATIONS TO HOLMIUM

by



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A THESIS

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The undersigned certify that they have read,
and recommend to the Faculty of Graduate Studies for
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ABSTRACT

Several experimental and computing techniques are described for use in the analysis of complex spectra and are applied to the spectra of neutral and singly-ionized holmium. A method for making electrodeless discharge lamps as a spectroscopic light source is given in detail. Results of the observed hyperfine structure and Zeeman effect in the Ho I spectrum are presented. A summary of the present states of analysis of the first and second lanthanide spectra is tabulated, and the NBS bibliography for the investigations of these spectra is updated.

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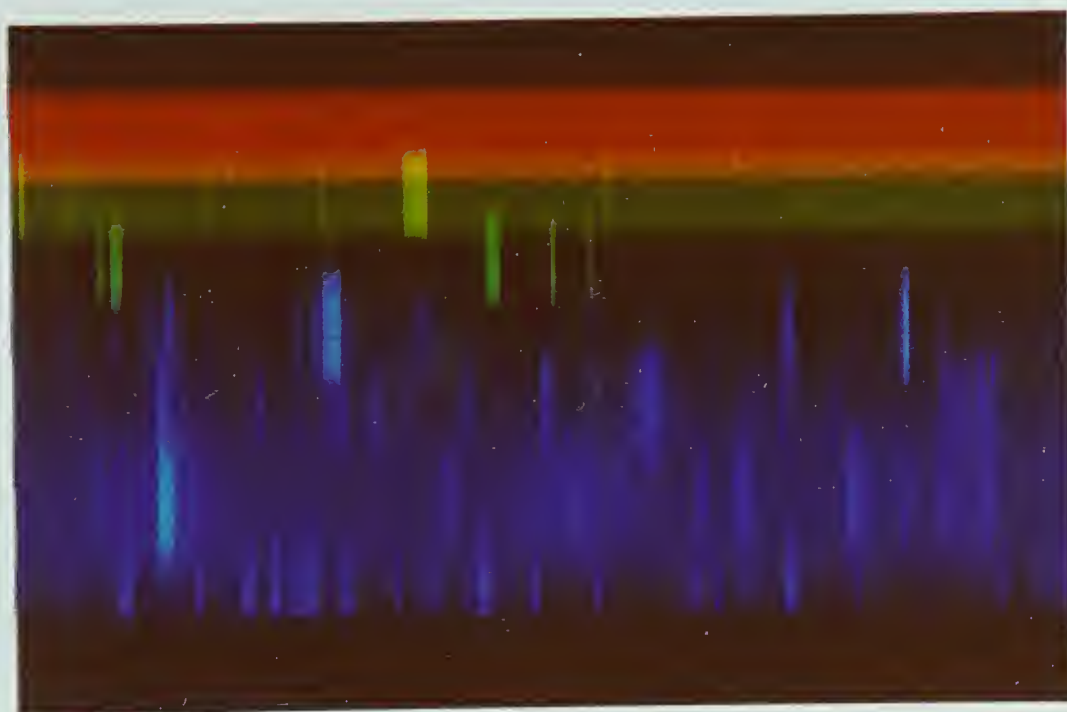


Figure 1

Section of holmium spectrogram
obtained using a high-blaze
grating in conjunction with
a predispersive element

ORDER
NUMBER

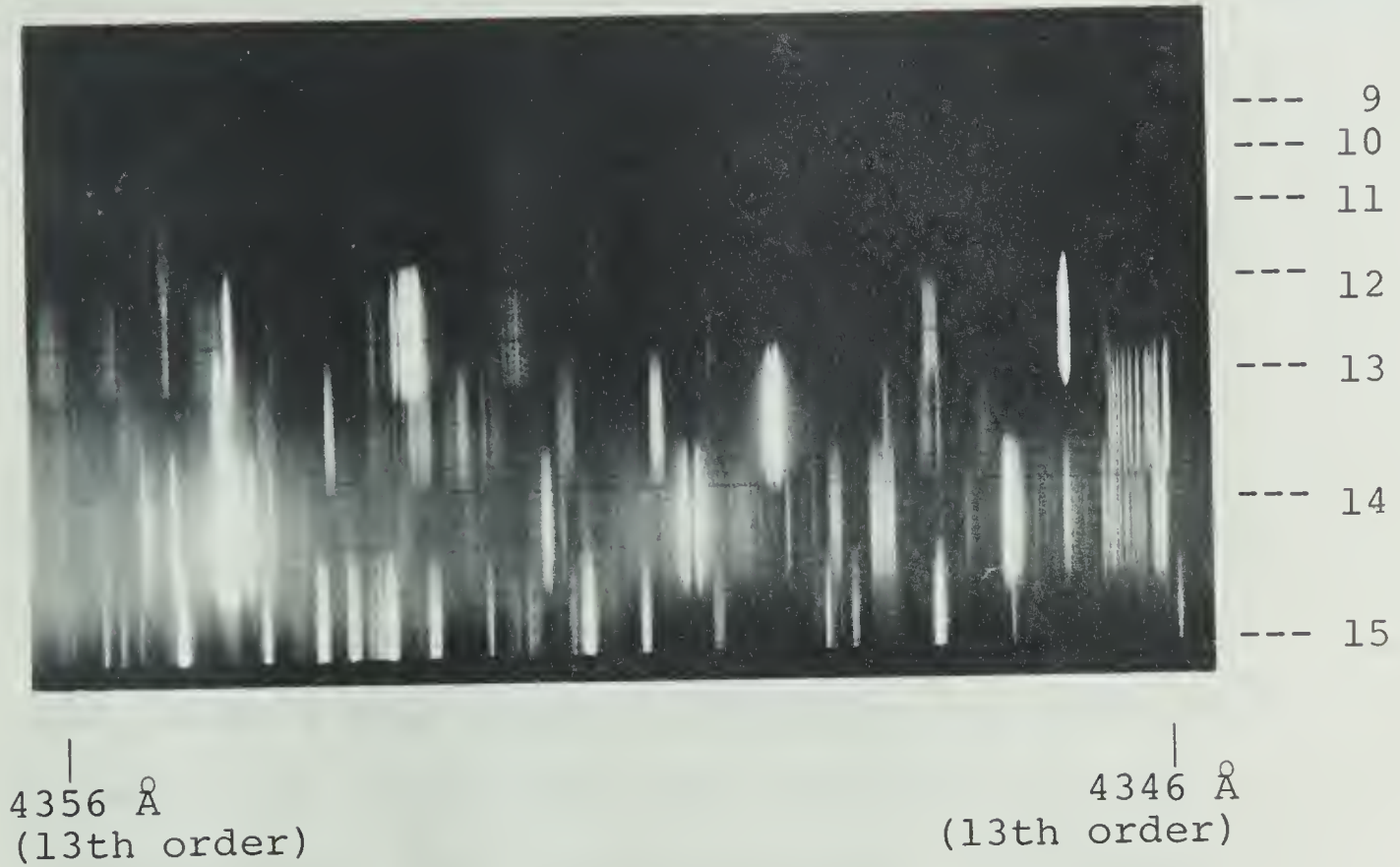


Figure 2

Holmium Spectrogram

(same region as figure 1)

Note: The orders toward the red
(9,10,11) are faint since the color
negative of figure 1 was used, and
the photographic paper here has
very low sensitivity in the red.

CHAPTER I

INTRODUCTION

1.1 Historical Background

The decade following the discovery of quantum mechanics (1925) saw a tremendous growth of theoretical and experimental work in atomic spectroscopy, for with quantum mechanics came the principles for the complete theory of atomic spectra. There arose a concerted effort among spectroscopists to provide a complete picture of all atomic spectra and, while a vast amount of knowledge for nearly all elements was accumulated, many analyses were very incomplete and some completely wrong. Following this rapid initial growth came a period of slower, methodical progress, subsiding considerably with World War II, during which non-military research was de-emphasized and most work was classified.

Today we are still experiencing the steady advancement of our understanding of atomic spectra, particularly with regard to rare earth spectra. A few decades ago quantities of rare earth samples of high purity were unavailable. They exist in

small abundances in the earth's crust, and at those times they were very difficult to separate due to their chemical similarity. Combining this with the high line population resulting from the many rare earth spectral terms and the breakdown of L-S coupling, the difficulties involved in rare earth spectral analysis were formidable. The past fifteen years, however, have witnessed the emergence of Racah's revolutionary theory for complex spectra, the development of digital computers for handling vast amounts of data, and the increased availability of larger quantities of highly pure rare earth metals, opening the way to investigation of this last relatively unknown group of elements.

As an illustration of the advancement in analyses of rare earth spectra during the last twenty or so years, a comparison of charts giving existing states of these analyses in 1946 and today appears in table 1. The number of separate spectra investigated has more than doubled, while the degree of analysis of each has grown tremendously. A more detailed summary of the present state of the rare earth spectra is given in the appendix.

TABLE 1

STATES OF ANALYSES OF THE LANTHANIDE SPECTRA
IN 1946 AND TODAY

(Rated from A to E in order of
decreasing extent of completeness)

1946 (1)					Today (2)			
Spectrum	I	II	III	IV	I	II	III	IV
Element								
58 Ce		B	B	C	B	B	A	C
59 Pr		C			D	B	B	B
60 Nd	C	C			B	B		
61 Pm					C	C		
62 Sm	C	B			B	B	C	E
63 Eu	A	B	E		A	B	D	E
64 Gd	B	B			B	B	C	
65 Tb					C	D		
66 Dy		D			E	C		
67 Ho					E	E	C	
68 Er					B	B		C
69 Tm	E	C			A	A	D*	
70 Yb	C	B	D		A	A	B	D
71 Lu	C	B	D		B	A	D	

* Inserted by author

1.2 Analyses of Holmium Spectra

The first reasonably accurate and useful list of holmium lines was that compiled by A.S. King (3) in 1930 (164 lines from 3837-4661⁰Å) as a part of his extensive investigations into temperature classifications of rare earth spectra. He refers to an earlier listing of holmium lines by Exner and Haschek (4), which contained many dysprosium lines as impurities. About ten years after King's publication came the Massachusetts Institute of Technology Wavelength Tables, cataloguing 800 holmium lines (without separation into first and second spectra), and extending the region covered to 2431-6694⁰Å. The latest published list is the National Bureau of Standards Table of Spectral Line Intensities, with about 900 holmium lines from 2500-8916⁰Å, all but 68 being assigned to the first or second spectrum. The main source quoted here is the work of Gatterer and Junkes (5), who apparently enlarged upon the Massachusetts Institute of Technology list up to 7000⁰Å, along with new National Bureau of Standards wavelengths above 7000⁰Å.

It is interesting to note the discrepancy in the National Bureau of Standards and Massachusetts

Institute of Technology tables below about 3000⁰Å. It appears that the National Bureau of Standards investigators have rejected some of the original identifications in this region and made some new ones as well, which is to be expected. Unfortunately, however, the latest editions of the Handbook of Chemistry and Physics have neglected this revision by the National Bureau of Standards (which is now nine years old), and still follow the old Massachusetts Institute of Technology list, including only 150 of its 800 lines.

Even with 900 lines known, the identifications of the first and second spectra of holmium are far from complete, since all rare earths are characterized by spectra containing many thousands of lines. The high density of lines can be appreciated when one notes that the ground configuration ($4f^{11}6s^2$) alone of holmium comprises 364 levels, and that there are several configurations within the energy structure of the atom.

The published spectral analysis of holmium beyond these wavelength identifications and spectrum assignments is almost nonexistent. A recent paper by McElaney (6) describes his work with Ho III: 9000

lines (only a few of these in the I, II, IV spectra) from 1900-11,000 \AA and 42 energy levels determined. Aside from this, neutral holmium has only three known levels, classified by their ground state transitions, while HoII has just two known upper levels with their transitions to the ground state and to one other low level. Work on the analyses of these two spectra is presently under way at the National Bureau of Standards (Zeeman Effect in the visible region), with nothing published as yet.

Theoretical predictions for holmium energy levels are scarce. Klinkenberg (7) has listed approximate levels for the ground state multiplet and for one other low multiplet, but little accuracy is claimed. Conway and Wybourne (8) list what are claimed as accurate values for the ground multiplet, and one is tempted to believe these since their accompanying calculations for the ground multiplets of dysprosium, erbium and promethium are in very good agreement with experimental results.

Belyanin (9) seems to claim discovery of the true ground multiplet levels simply through the method of constant differencing and quotes them as being 0, 4664, 8758, 12541 cm.^{-1} for the $^4\text{I}_{\frac{15}{2}, \frac{13}{2}, \frac{11}{2}, \frac{9}{2}}$

levels respectively. It is strange that Smith and Wybourne make no mention of these results for experimental comparison to their calculations. Perhaps they noted that Belyanin has omitted stating which transitions characterize these levels and also that there seems to be no agreement between pairs of known holmium transitions and these purported energy separations (at least, the present author has found no such agreement using normal computer searching programs to be discussed later). Yet there seems to be no obvious fitting of known transitions to the approximate levels proposed by Smith and Wybourne either.

This highly incomplete state of spectral knowledge for neutral and singly-ionized holmium was the primary motivation behind the choice of this element for the application of spectral analysis techniques. It was hoped to be able to discover reasons for the inability of previous investigators to even partially unravel the holmium energy level system, as well as to extend the published spectral knowledge of holmium and provide basic data for more extensive investigations beyond this project.

1.3 Astrophysical Importance of the Rare Earths

Perhaps the most frequent application of rare earth spectral knowledge is in the identification of stellar spectra. Hundreds of stellar lines in spectra of various types remain unidentified and the rare earths likely comprise a large portion of these since their spectra are still the least known of any group of non-radioactive elements.

The rare earth elements appear predominantly in all of the cooler "peculiar" stars (Ap stars) (10). These stars, which possess measurable magnetic fields, are characterized by large overabundances (relative to the Sun) of silicon, manganese, strontium, or the rare earths, especially europium, those of the rare earths being largest of all. An outstanding example is Przybylski's star (HD 101065) (11), the spectrum of which contains only a few lines of hydrogen and calcium along with many very strong rare earth lines, including some extremely strong lines of holmium and dysprosium. This star is thought to be cooler than most Ap stars, whose temperatures range from about 8000°K to 15,000°K. It is likely that in higher temperature Ap stars the rare earths (with fairly low ionization potentials) exist largely as two or three times

ionized atoms. There are, however, large variations among the observed spectra. These could be explained by temperature variations of a few thousand degrees resulting in dramatic changes in the relative amounts of the various ionization states. In general the understanding of the phenomena involved in these rare earth overabundances remains a major problem in astrophysics.

With the investigation of rare earth lines in the Sun fairly well advanced (12), the detailed study of the rare earths in other stellar spectra is just beginning. Further work, especially on the singly and doubly ionized rare earths, is desired here, now that direct access to regions beyond the earth's atmosphere provides much wider spectral ranges for the astrophysicist.

1.4 Description of Present Project

The present research project consisted of three parts: (a) a background survey on spectral analyses of the lanthanides; (b) the making of electrodeless lamp sources and their use in obtaining line spectra and Zeeman patterns of holmium; (c) the application of certain techniques of spectral analysis to the spectrum of holmium.

During the course of investigating the present states of analysis of the first and second lanthanide spectra, it was decided that a comprehensive bibliography of all recent analyses of these spectra was badly needed, none having been published for about seven years. Shortly following the completion of this bibliography a publication was released by the National Bureau of Standards (Special Publication 306-4) which included an extensive bibliography of all lanthanide and actinide spectral investigations up to and including 1968. The present author's listing was therefore revised to include only additions to this bibliography and extend it up to July 1970. These additions appear in the Appendix.

As was mentioned previously, the choice of holmium for experimental investigation was based upon the complete lack of published Zeeman Effect data on it and the gap it formed in the knowledge of electron energy level structures of the lanthanides. The obtaining of successful electrodeless lamp sources made up a major portion of the experimental work. With these lamps, dozens of photographs were taken of line spectra and Zeeman patterns using different gratings, at various dispersions, and under many

different operating conditions, all in the process of learning experimental spectroscopic techniques leading up to eventually obtaining useful Zeeman spectra of holmium.

The spectral analysis techniques were applied mainly to neutral holmium. The reasons were that in general the neutral spectrum is favored in the emission from electrodeless lamps, and that the time allotted for the present project was limited. Computer programs were developed for the sorting of wavenumber differences of known lines to provide a breakthrough into the energy structure of the atom. The observed hyperfine and Zeeman patterns would then be useful for verification of proposed levels, as well as providing structural details about these levels. With a basic level structure available, it should be possible to analyze many of the resolved Zeeman patterns of lines complicated by hyperfine structure. The programs were first tested by using them to fit lines of neutral thulium to a known level scheme. Following this, they were applied to neutral holmium. Finally, an attempt was made to extend the level structure of singly-ionized holmium (Ho II) by building from the two known intervals.

CHAPTER II

ELECTRONIC STRUCTURE AND SPECTRA
OF THE LANTHANIDES2.1 Shell Structure

The rare earth elements consist of two groups of 14 elements each, the lanthanides and the actinides, characterized by the progressive filling of the 4f- and 5f-shells respectively of their electronic configurations. The actinides will not be considered here, although the extensive resemblance of their electronic structures to those of the lanthanides allows application of many general properties to both groups almost without modification.

The neutral lanthanides include the elements from cerium ($Z=58$) to lutetium ($Z=71$). Their electronic structures represent a breakdown in the expected shell sequence in the periodic table, with the building up of the inner 4f-shell after the initiation of the 5d-shell by lanthanum ($Z=57$). In fact the 5d-electron is even replaced by an additional 4f-electron in all the ground states of the lanthanides except for cerium (single f-electron),

gadolinium (half-filled shell of 7 f-electrons), and lutetium (filled shell of 14 f-electrons). Thus the outer electrons are either $5d6s^2$ or just $6s^2$, the inner 4f-shell being shielded, which explains the strong similarity in chemical properties of all the lanthanides. More specifically, the 4f-shell behaves as an inner shell due to the contraction of the potential well for the f-eigenfunction, so that its maximum lies inside the $5s^25p^6$ closed shells of the xenon structure. This "lanthanide contraction" allows the f-electrons to be shielded by the s^2p^6 closed shells as well as reducing the penetration of the f-eigenfunctions beyond the outer shells, both preventing any strong interaction of the f-electrons with their external environment.

The f-electrons do however provide a basis for the complex spectral characteristics of the lanthanides. With two or three electrons outside the $4f^n$ core of the neutral atom, many combinations are possible which yield configurations of spectroscopic interest. For example, in neutral gadolinium 13 configurations have been established experimentally (13) involving various combinations of 5d, 6s, 6p, and 7s electrons with an f^7 or f^8 core. More than 1200 lines have been

assigned to 545 levels arising from these configurations. The ionized atoms of the lanthanides normally exhibit far fewer configurations. Nearly all possess either a single electron or no electron outside the $4f^n$ core, greatly reducing the possible number of configurations.

2.2 Characteristics of Lanthanide Spectra

A peculiarity of the lanthanide structure is the approximate equality of binding energies of the 4f- and 5d-electrons. This situation has caused uncertainty in the ground configurations of several of these elements. Overlapping between the competing configurations $4f^n 6s^2$ and $4f^{n-1} 5d 6s^2$ combined with inability to connect them either directly or indirectly by transitions has often led to the development of two independent term systems. Direct transitions between these systems lie in the inaccessible infrared region, while indirect connection through higher levels has usually awaited gradual extension of analyses to these higher levels. However, the ground states of all the lanthanides have now been established (14), with the exceptions of Tb I (15) and Tb II (16). In Tb II both term systems have been partially constructed but remain unconnected; in Tb I the $4f^8 5d 6s^2$ system is partially

known while the $4f^9 6s^2$ system is as yet undiscovered. The extension of wavelength identifications farther into the infrared region will likely resolve this difficulty in the near future.

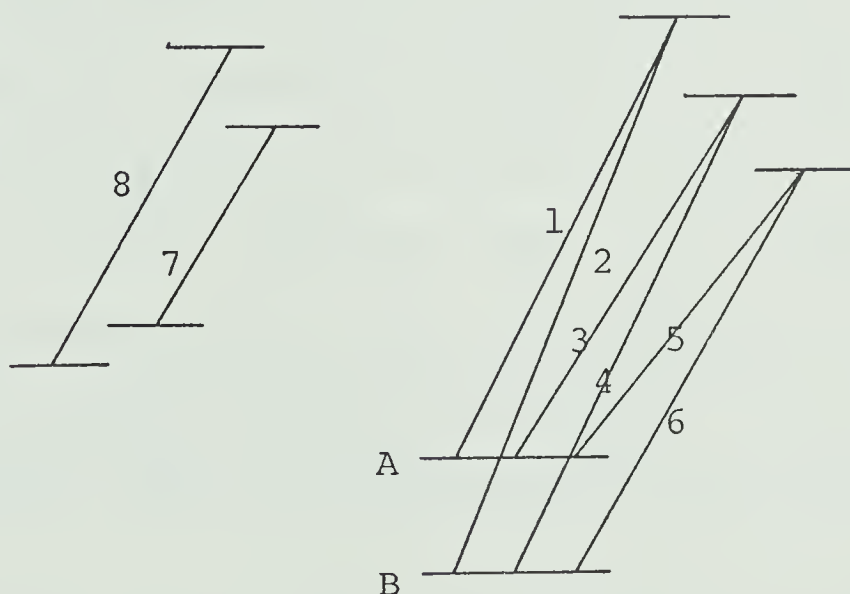
There are further problems associated with the analysis of rare earth spectra. The large quantum numbers describing the energy levels result in very strong diagonal transitions with relatively weak off-diagonal transitions. This means there are fewer real intervals between pairs of high intensity lines. Also, variation from LS coupling theory causes real intervals to occur mostly between lines of very different intensities. This situation dictates that weak lines as well as strong have to be taken into consideration from the beginning of the analysis. A further result of the breakdown of LS coupling is the establishing of connections between multiplets of different multiplicity, that is, the loss of S as a good quantum number. Finally, many rare earth spectra are observed not to follow the Landé interval rule, which states that the relative separations of the fine structure levels of a term are proportional to the j -values of the upper levels involved in each separation. This again is due to the breakdown of

LS coupling. The result is that certain regularities which can normally be included in computer programs to establish new levels are not available in rare earth spectra.

A final, but very serious, problem to be overcome in analyses of rare earth spectra is due simply to the high line population that characterizes such spectra, over 25,000 lines being known for some elements. Handling so many lines represents a formidable task in itself, even when only a few hundred lines are considered at one time. When weak lines as well as strong lines must be looked at together, as has often been found necessary, the problem can become insolvable, even for the computer.

To see why this is so, one notes that the first goal in any spectrum analysis is to establish a limited electron energy level structure with reasonable confidence. This is usually done by converting the wavelength of each line in the spectrum into units which specify the magnitude of the energy of the transition that it represents. The unit used is the wavenumber (cm^{-1}), this being the energy of the transition divided by hc (h is Planck's constant,

c the speed of light). Then the combination principle is applied to the list of wavenumbers. This involves simply searching the list for pairs of wavenumbers that have a given difference. If a particular wavenumber difference appears a number of times between several pairs of wavenumbers, it likely represents a real interval between two energy levels in the electron structure of the atom. The sketch below illustrates how pairs of transitions from several common levels may terminate on the same two final levels, thus giving the set wavenumber pairs with the difference corresponding to this interval.



$$(A-B) = (2-1) = (4-3) = (6-5) = (8-7)$$

The entire level structure must adhere to this combination principle. The situation is complicated, however, by the appearance of wavenumber differences which are equal to real intervals, yet are formed between wavenumbers without a common level (see the above sketch). These chance occurrences decrease the usefulness of the combination principle for large line lists, since the probability of the chance occurrence of any given difference increases as more lines are considered. With a few levels established, the extension to further levels then follows more easily, in principle at least.

However, if an initial level structure cannot be formed even through the use of an abbreviated line list representing common characteristics of such properties as intensity, self-reversal, hyperfine structure, or Zeeman patterns, there is no alternative but to use a fuller line list. The degree to which the number of purely random coincidences may obscure the significant data is illustrated by the following example.

Using 500 strong lines spread more or less uniformly over the usual photographic range (2500-7000Å) and measured with the usual accuracy ($\pm 0.01\text{\AA}$), one can

expect about one pair of lines to form a given wave-number difference by chance. A real difference will be given by up to a dozen or so pairs of lines and thus be easily seen. The random coincidences in such a difference can be recognized when they remain isolated and unrelated to other levels as the structure is developed. However, should it be necessary to include a much fuller spectrum with, say, 5000 lines one can expect about 100 chance pairs to form any given wave-number difference. Here it is impossible to pick out significant differences from chance coincidences, and the combination principle alone yields nothing. This problem, which is well known in the rare earth spectra, points out the need for obtaining more information about the lines. The Zeeman effect is usually the best way of achieving this.

2.3 The Use of Hyperfine Structure and Zeeman Effect in the Analysis of Complex Spectra.

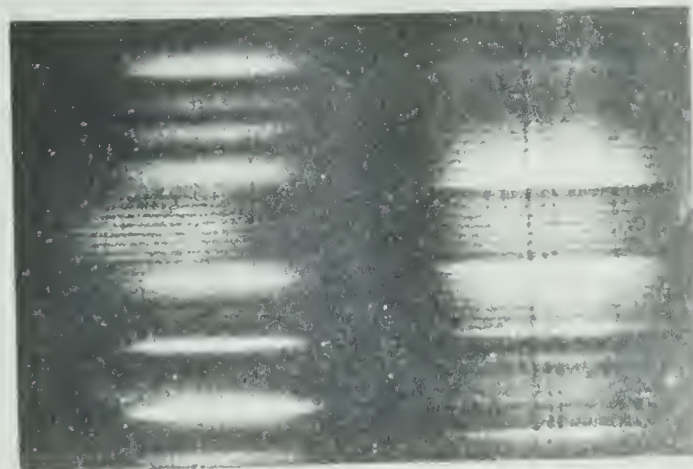
The energy levels of an atom or ion whose electrons are moving in a purely central field are $(2J+1)$ -fold degenerate. This degeneracy may be removed by the introduction of an external noncentral field. When a magnetic field is used the result is

called the Zeeman effect. The degeneracy may also be removed without the application of an external field. Atomic nuclei with either odd nuclear mass number or both odd atomic number and even mass number have nonzero nuclear spin. This nonzero spin gives rise to a nuclear magnetic-dipole moment and, for spin greater than one-half, an electric-quadrupole moment as well. The interaction between these nuclear moments and the spin and orbital moments of the electrons produces a splitting of the energy levels which is known as hyperfine structure.

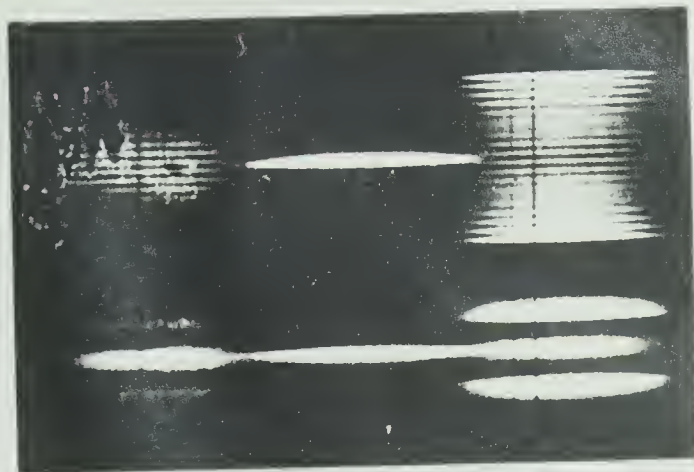
Hyperfine structure is apparent to some degree in most of the lanthanides, with wide patterns appearing in the spectra of those elements having large nuclear moments (holmium, praseodymium, europium, promethium, and lutetium). A section of the holmium spectrum appears in figure 3 , illustrating the variety of patterns observable. Such well-resolved hyperfine structure can often be directly analyzed to help confirm and extend known level structures. It is generally less useful than the Zeeman effect, however, since it yields less, and often less accurate, information about each level. Unfortunately, the same hyperfine patterns which are useful for analyses of



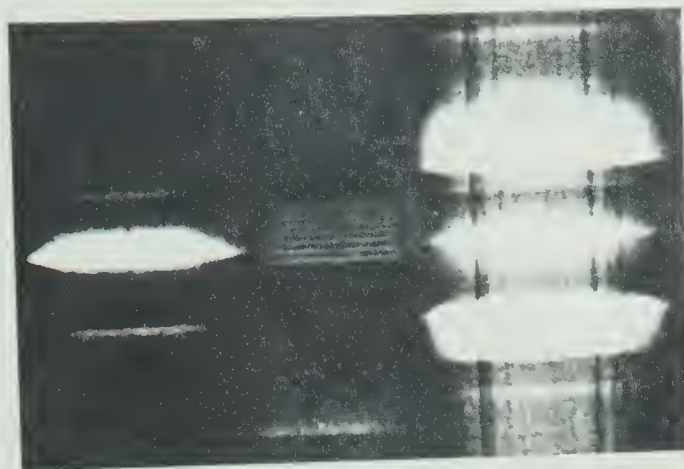
Figure 3
Hyperfine structure in the holmium spectrum



(4594.02 Å)
Figure 4
Zeeman pattern of
Eu I impurity line



(4222.29 Å) (4223.47 Å)
Figure 5
Resolved and unresolved
Zeeman patterns of Ho I



(6133.60 Å)
Figure 6
Zeeman pattern distorted
by hyperfine structure

line spectra become a hindrance in Zeeman spectra. Depending on the width of the hyperfine structure, it can result in as little as a slight broadening of the Zeeman components or as much as the complete obscuring of the Zeeman pattern. The two extremes are displayed for Ho I in figure 5 for the line 4223\AA and in figure 6 for 6133\AA .

(a) Hyperfine Structure

The simplest way to utilize hyperfine patterns alone in a term analysis is to base the selection of wavenumbers to be searched for repeating differences upon the total width of the pattern or the direction of shading. Giachetti (17) successfully established the first levels of protactinium by looking for repeating wavenumber differences among lines with wide splittings. The same procedure yielded a preliminary level structure in doubly-ionized praseodymium for Sugar (18). Meinders (19) used recurring differences between lines having opposite direction of shading to detect some basic levels in terbium. A more refined procedure, also described by Meinders, is to invoke the requirement that pairs of lines having a constant wavenumber difference also must have a constant difference in the width of their hyperfine patterns, if any. This is

valid since the subtraction of one pattern width from the other exactly cancels the effect of the hyperfine structure in their common level, leaving only the contributions from the levels forming the interval, and this is common to all genuine pairs giving that interval. Provided that one can obtain a sufficient accuracy in the pattern measurements, this criterion provides a stringent basis for the acceptability of common wavenumber differences. Yet another method is to group lines according to the magnitude of their total hyperfine splitting and then seek common ratios of spacings between components to establish which lines originate from, or terminate on, common levels. Here also a high measuring accuracy is required before the ratios of spacings will give any dependable results. This method is particularly useful for grouping transitions to or from levels distinguished by abnormal structure, usually the result of deviation from the interval rule due to a large nuclear quadrupole moment. Davis has applied this procedure to terbium (20). In general, hyperfine structure analyses are more fruitful in the second spectra of the lanthanides than in the first simply because of the greater abundance of resolved hyperfine patterns. This is mainly because the ground

configuration of all the singly-ionized lanthanides, except for lutetium, consists of either a single 6s-electron or a 5d- and a 6s-electron outside the f^n core. Such an unpaired s-electron, with a deeply penetrating orbit, interacts strongly with the nucleus and gives the widest hyperfine structure. The neutral lanthanides on the other hand have mostly $4f^n 6s^2$ configurations in the ground state, with no unpaired s-electron and consequently little or no hyperfine structure in ground levels. Several of their excited configurations can display hyperfine structure though.

(b) Zeeman Effect

The particular value of the Zeeman effect for term analysis of complex spectra lies in (i) its application to a known level system, based upon the combination principle, for the confirmation of accepted classifications and the further interpretation of levels by providing g-values; (ii) its use in sorting the enormous volume of unclassified transitions characteristic of highly complex spectra by specifying detailed properties of the two levels involved in each transition. If a very extensive Zeeman spectrum of complete and well-resolved patterns can be obtained for an element, the data can be readily analyzed using a large computer, by comparing

wavenumbers, J-values, and g-values simultaneously. However, if only a part of the Zeeman spectrum is available, or particularly if complications such as distortion by hyperfine structure or self-reversal are encountered, or if the resolution is insufficient (due to insufficient resolving power of the spectrograph, too weak a magnetic field, or both), the amount of analysis that results from the Zeeman effect can be greatly reduced.

A particular disadvantage of the Zeeman effect applied to complex spectra is that the abundance of spectroscopic terms of high L and low S gives most levels a g-value close to unity. Hence differences in g-values are small and patterns tend to be unresolved. In the lanthanides this applies to all but the simplest structures, and produces Zeeman spectra with as many as 90% of the patterns unresolved, as reported for terbium (20) and for holmium in the present project. The only solution here seems to be the use of much higher field strengths, preferably high enough to produce the Back-Goudsmit effect in which the usual Zeeman effect results but where each Zeeman component has its own hyperfine structure. One is always limited, however, by the Doppler width of the lines, which for holmium is about 0.05 cm^{-1} (width at half intensity) at 5000\AA , assuming a temperature of

around 3000°K in the source. If we require a line separation of, say, 0.06 cm^{-1} to resolve two such Doppler broadened lines, for a field of 28 kilogauss this corresponds to being able to resolve a pattern having Δg no less than 0.05 Lorentz units, but only if there is no hyperfine structure present. In practice, for Ho I with a field of 28 kilogauss the smallest Δg that yielded good g -values from a pattern was 0.165 Lorentz units, though one pattern displayed good resolution of the π -components with Δg only 0.10 Lorentz units (its σ -components were unresolved). For most lines the additional broadening due to hyperfine structure is sufficiently great that their Zeeman patterns are not resolved even though the limit imposed by the Doppler broadening has been met.

The most useful data from the Zeeman effect is yielded of course by fully resolved and complete patterns, from which it is always possible to obtain the J - and g -values of both levels involved. Yet even totally unresolved patterns can contribute some information about the J - and g -values which can be helpful in a term analysis. Below are summarized the methods of interpreting Zeeman patterns.

Fully Resolved Patterns

- (1) The separations of the π -components and σ -components are used to give Δg , and the number of components yields the J-values.
- (2) Using the Δg value and the J-values, one can solve for the g-values.

Partially Resolved Patterns

- (1) Symmetrical patterns ($J_x = J_y$)
 - (i) If the π -components are resolved, their separations give Δg . J is found from the number of π -components. If all the π -components are not visible, J may still be found by interpolating inwards from the strongest component.
 - (ii) If the strongest σ -components can be identified, using J and Δg one can solve for the g-values.
- (2) Shade-in σ patterns ($J_x > J_y$; $g_x > g_y$)
 - (i) If the π -components are resolved, their separations give Δg .
 - (ii) If all the π -components are visible, J_x and J_y can be found.
 - (iii) If the strongest σ -components can be identified, J- and Δg -values may be used to solve for the g-values. (This

will normally be the case if (i) and (ii) are satisfied, unless the pattern is partially masked or is partially distorted by hyperfine structure.)

- (3) Shade-out σ patterns ($J_x > J_y$; $g_x < g_y$)
(analysis as for shade-in patterns)

Notes

The g -value calculation requires a knowledge of which are the strongest σ -components, but other pairs of σ -components may be more suitable for the actual calculation due to their sharpness or isolation from blending.

Occasionally, when a pattern is partially resolved or blended, the π -components are obscured and less reliable than the σ -components. In these cases Δg should be based upon the interval between adjacent σ -components.

If $J \neq 0$, an incomplete pattern does not reveal the J -values, since the numbering of the individual σ -components is unknown. However, one can set a lower limit on the lesser J -value by counting those components that are visible.

Unresolved patterns

(1) Sharp triplets

The g-values are equal or very nearly equal and this value (or actually the mean value of the two) is equal to the σ -separation.

(2) Slightly fuzzy triplets

These are less reliable than sharp triplets, but if $\Delta J = 0$ one can still estimate a mean g-value using the symmetry about the strongest σ -components. This procedure is not so accurate for the asymmetrical, shaded σ -components representing $\Delta J \neq 0$ transitions.

(3) Unresolved patterns that have definitely shade-in or shade-out σ -components yield $\Delta J \neq 0$ and indicate whether the level with higher J has the larger or the smaller g-value.

(4) If the σ -components do not display asymmetrical shading and the π -components appear as one sharp pair of lines, it is likely an unresolved $\Delta J = 0$ pattern.

- (5) If the σ -components are unresolved but the maximum and minimum separation boundaries are clearly shown, a mean g-value can be roughly taken as one-half the sum of these maximum and minimum σ -separations.

CHAPTER III

APPARATUS AND EXPERIMENTAL PROCEDURE

3.1 Apparatus

The light source used for all observations was the electrodeless discharge lamp, to be discussed in section 3.2, which was excited by a Raytheon Microwave Power Generator operating at 2450 megacycles per second with a full-wave (12 cm.) resonant cavity (fig. 8). The cavity was air-cooled and tuneable for maximum efficiency, that is, minimum reflected power for any chosen input power, both of these being measured on meters.

For Zeeman Effect investigations an electromagnet (fig. 7) from Pacific Electric Motor Company, Oakland, California was employed. The poles were fitted with 1" diameter tapered pole caps adjusted to a 1.25" gap. A field of about 30 kilogauss was attainable operating the magnet at full power, but running at something over half of full power (800 amperes) a field of about 27 kilogauss resulted, the latter setting being used to avoid overheating the power supply at a sacrifice of only 10% in field strength.

A 3.4 meter Ebert spectrograph was used with a 7500 l.p.i. grating blazed for the ninth to twentieth orders in the range 6000\AA to 3000\AA . The linear reciprocal dispersion obtainable in the tenth order was 0.5 \AA/mm .

The optical system (fig.9) consisted of a front-surfaced concave mirror (diameter=6", f=60.5") which reflected the light from the microwave cavity through a Wollaston prism, an order sorter (21), and a lens onto the spectrograph slit.

The 2 cm.-square Wollaston prism separated the components parallel (π) and perpendicular (σ) to the field, while the order sorter (fig.9) separated the overlapping orders, allowing several orders to be photographed simultaneously. The lens very near the slit served to control illumination of the grating, correcting the slightly off-horizontal beam path which was introduced to accommodate the order sorter.

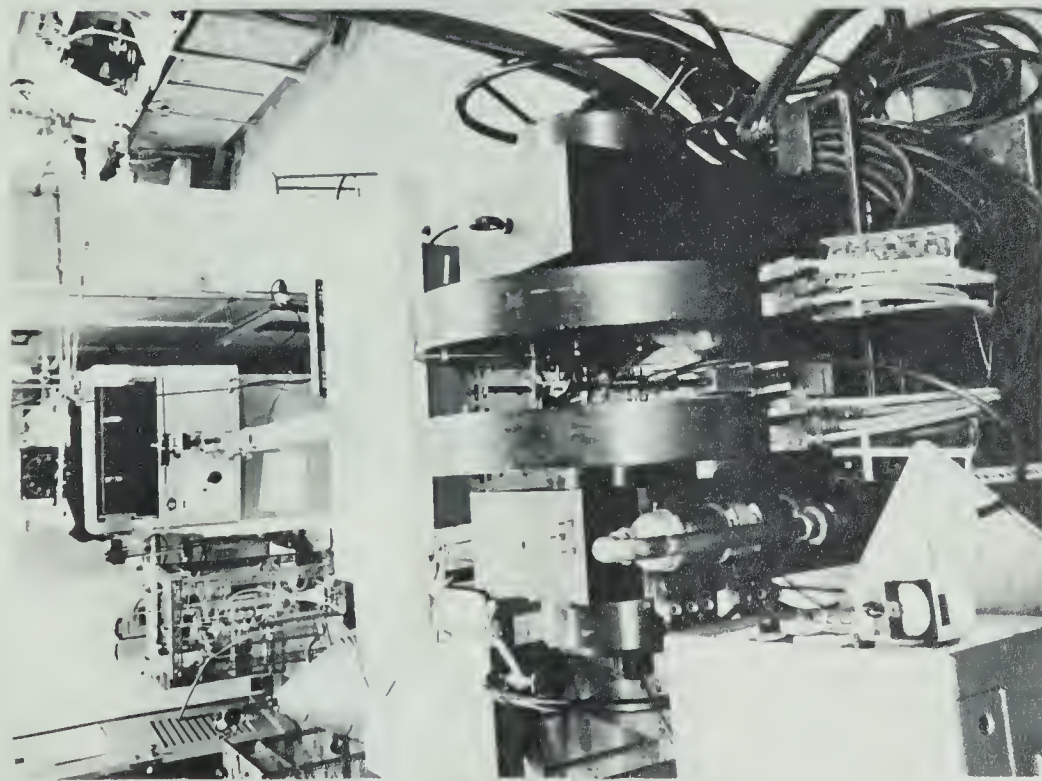


Figure 7

Microwave generator, electromagnet,
and spectrograph



Figure 8

Microwave cavity containing lamp
inside electromagnet

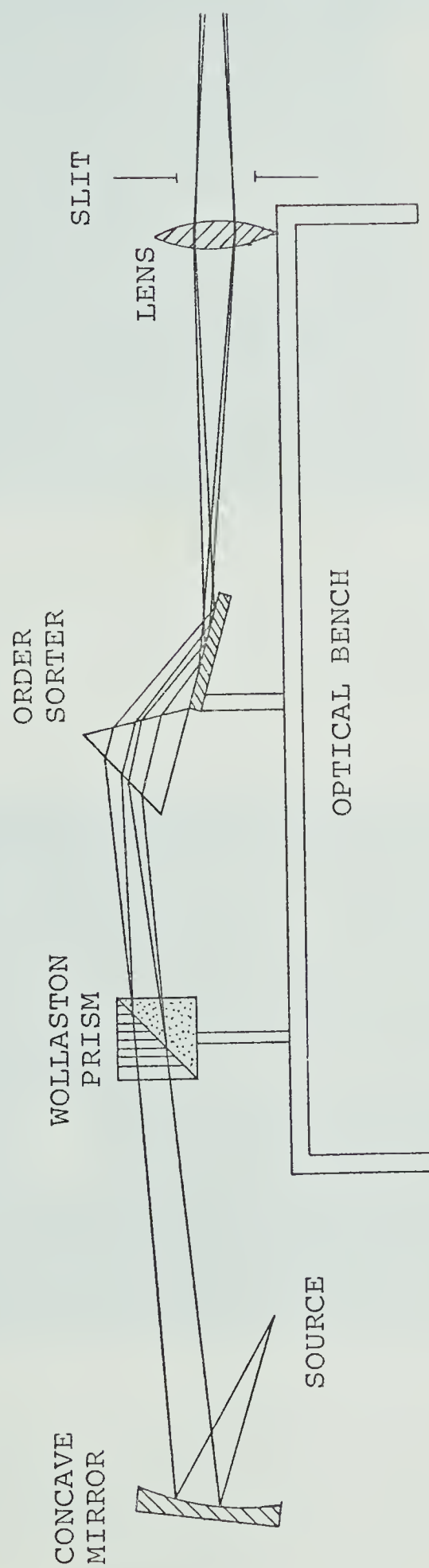


Figure 9

SCHEMATIC OF OPTICAL SYSTEM

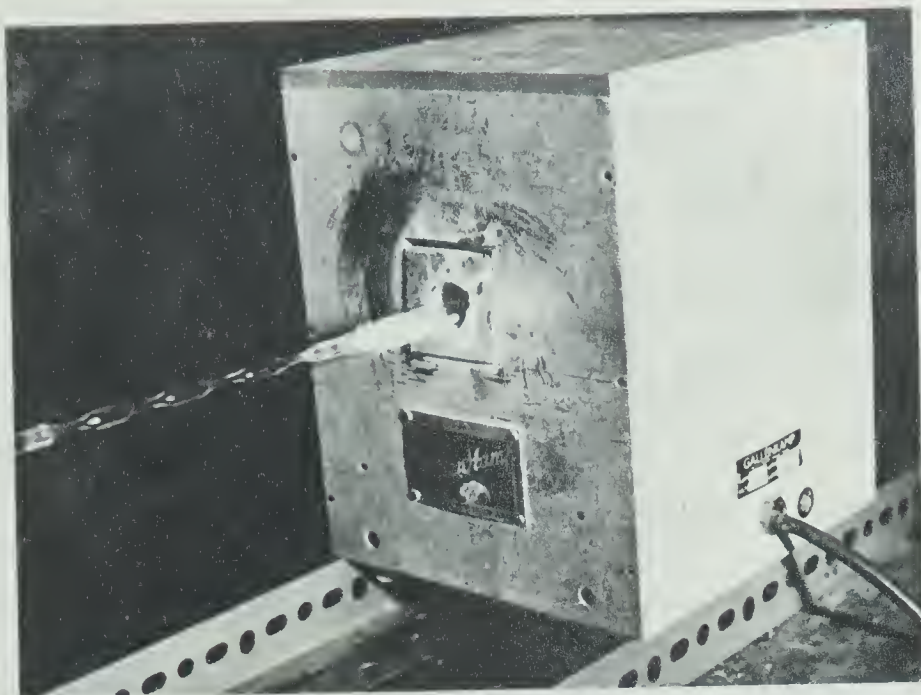


Figure 10

Sample tube containing preparation tube,
with oven removed

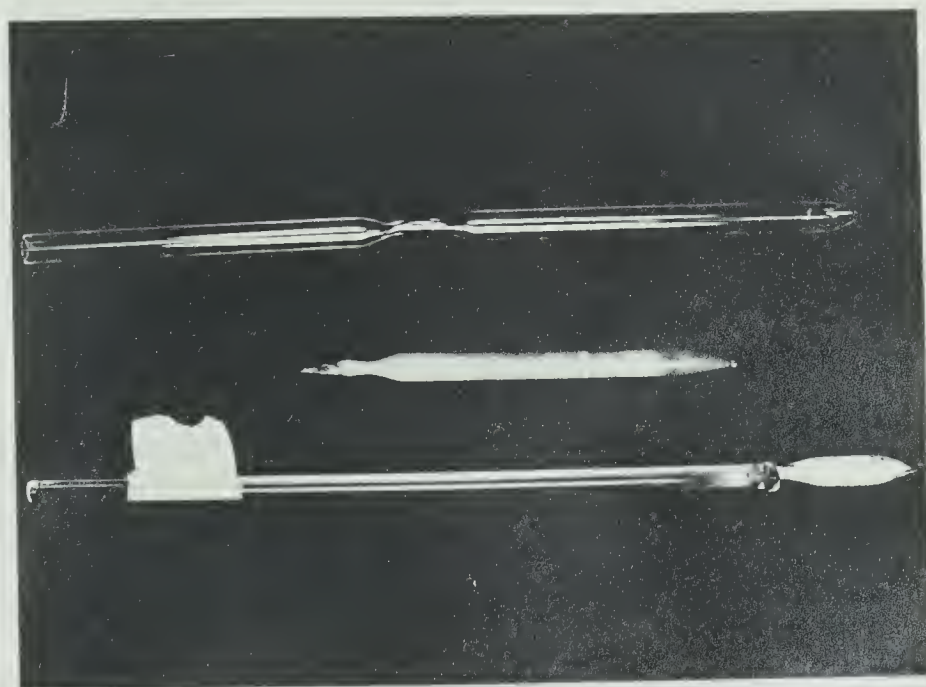


Figure 11

Examples of a preparation tube before use and
after sealing and baking, and a final lamp
attached to a quartz rod

3.2 Manufacture and Operation of Lamps

The electrodeless discharge lamp is generally accepted (22)(23) as the most efficient light source for the study of complex spectra, in particular the lanthanides and actinides. The primary advantages of these lamps are that they emit sharp, high intensity lines and that the first spectrum is favored. The low pressure and moderate temperature at which they operate yield the sharp lines. The favoring of the first spectrum is important, since arc sources normally excite mainly lines of ionized spectra, particularly in strong magnetic fields. This phenomenon, known as magnetic enhancement, is also apparent in the electrodeless lamp sources (24), though to a lesser degree than in the arcs. In addition the second spectrum can be enhanced simply by pressure of the metal in the lamp (23). Further advantages are their ruggedness, small volume, and conservation of sample, the last being attractive for investigations of uncommon metals such as the rare earths. Hence the electrodeless lamp appears to be the ideal light source for Zeeman Effect observations of the first and second spectra of the rare earths.

The procedure for making the electrodeless discharge lamps is fairly standard (23). Briefly, pure holmium metal and pure iodine are introduced into a quartz tube (5 mm. internal diameter) which is evacuated to the vapor pressure of iodine (0.25 mm. Hg. at room temperature), sealed, and baked in an oven for several hours to form holmium iodide (HoI_3). The cooled preparation tube is then re-opened at one end and sealed inside a larger quartz tube which has been joined to the final sample tubes (see figure 10). Following evacuation to 10^{-5} mm., the iodide is sublimed from the preparation tube into the sample tubes. These are individually sealed off to form the final lamps. This general procedure appears to be reasonably successful and adaptable to the making of lamps of various sizes, concentrations, and pressures. However, the overall efficiency was found to be lower than anticipated. Out of more than 100 lamps made, only about 15 were long-lived and of high intensity. Continued use of electrodeless discharge lamps as a light source would certainly justify a separate detailed investigation of more efficient utilization of this procedure.

The amounts of metal and iodine initially placed in the preparation tube were decided by testing the procedure using several different holmium-iodine ratios at several different total concentrations. The most successful results were obtained using 20 mgm. of holmium with 30 mgm. of iodine, and these amounts were used for all subsequent lamp making operations. The preparation tubes were attached to the vacuum system simply with thick-walled rubber tubing (internal diameter 4mm.), since the vacuum attainable here was limited to the vapor pressure of the iodine and hence a high vacuum seal was unnecessary. After sealing it under vacuum, the tube was baked in the oven. Both successful and unsuccessful tubes were obtained at oven temperatures of about 600 - 1000°C, so that no optimum temperature was evident. Baking times were normally six hours. A more complete reaction was found to occur in the preparation tube if it was allowed to heat up along with the oven, avoiding rapid vaporization of the iodine.

The sample tube preparation required a more involved procedure. Since operating temperatures of the final lamps exceeded the melting point of

normal pyrex, all tubes were made of quartz. Also, high vacuum conditions were necessary for preparing the final tubes. These two requirements were most conveniently met by having a set of graded seals made between short quartz tubes and pyrex socket joints. Thus the final sample tube, formed separately from quartz tubing, was simply sealed onto the quartz end of the graded seal junction, the graded seal being re-usable. The tip of a preparation tube was then broken open and the preparation tube was inserted into the large open end of a sample tube, which was immediately sealed, attached by the ball and socket joint to the vacuum system, and evacuated. During evacuation, the end containing the preparation tube was covered by a wet cloth while the remainder of the sample tube was cleaned by periodical heating with a torch and exciting with a Tesla oscillator. Evacuation was continued until the torch and Tesla treatment could not boost the pressure over 1×10^{-4} mm. Hg. Lowest stable pressures attained were normally 3 to 5×10^{-5} mm. Hg. Evacuation times varied from two to five hours, depending on the amount of unreacted material in the preparation tube.

Once a sufficiently low pressure had been reached

the pre-heated oven was slid over the sample tube to enclose most of the central section with the constrictions, as well as the end with the preparation tube. Only a few minutes or less were required to sublime the holmium iodide into the final sample tube, after which the oven was removed and the end containing the exhausted preparation tube drawn off using a torch. Evacuation was continued until the pressure returned to about 5×10^{-5} mm. (usually a short time), the iodide being distributed by torch as desired among the final small tubes. Finally, each of these tubes was carefully removed by attaching a quartz support rod to the end and drawing off the lamp. As many as four lamps at a time were obtained by this procedure, though as a rule only one or two high quality ones resulted from each good sample tube. The most critical point appeared to be the judgment of how much one should distribute the sublimed iodide by torch in the final sample tube. The best lamps contained a considerable amount of the whitish iodide.

The most successful lamps usually required either pre-heating by torch or pre-cooling in liquid nitrogen prior to lighting in the microwave cavity using Tesla

excitation. Lamps which lit spontaneously in the cavity or immediately upon excitation were usually, but not always, too dim for use as a light source. Care was necessary to assure sufficient air cooling of the cavity once it was tuned for maximum efficiency, since high intensity operation resulted in very high lamp temperatures. On occasion a good lamp operating at maximum brightness would be punctured by atmospheric pressure on the weakened hot quartz, a most disheartening occurrence.

The difficulty encountered in trying to light the lamps with the microwave cavity between the pole pieces of the magnet eventually led to the lighting of lamps outside the magnet and then insertion of the microwave cavity with lamp operating into the magnet cavity. On occasion the lamp went out upon insertion into the field, but the method, with patience, was successful.

The greatest problem encountered with regard to lamps was their useful lifetimes. Most of the best lamps operated stably at high intensity only a few times before they began to turn reddish-brown on the inside and would no longer light. The holmium iodide appeared to have dissociated in these cases,

leaving the lamp useless. However, this occurrence was never predictable and a few of the best lamps lasted for many hours of successful operation, with and without a magnetic field, before succumbing. Here again one appreciates the need for further study of the peculiarities of electrodeless discharge tubes.

3.3 Photographic Plates and Their Measurement

The following exposures were obtained with holmium: spectrum only, nearly all of the region 3600-9000Å; Zeeman patterns, nearly all of the region 4100-6800Å. Kodak 103a-F plates were used for the spectrum from 3600-7000Å and for all the Zeeman patterns, while Kodak I-N plates were needed from 7000-9000Å.

Wavelength identifications of the spectra were based on holmium lines listed in the National Bureau of Standards Table of Spectral Line Intensities, with occasional use of the Massachusetts Institute of Technology Wavelength Tables for weaker lines. A comparison spectrum of neon taken at the same settings provided initial identification of the wavelength region appearing on the plate. Photographs were nearly always taken at three pre-deter-

mined grating angles, for which accurate dispersion curves had been graphically plotted previously in this laboratory.

Measurements of Zeeman patterns were made on a Zeiss spectrogram comparator, with all patterns being measured at least three times to eliminate any personal errors. The separations in microns of the Zeeman components in each pattern were converted into Angstrom units using the dispersion graph. These intervals were then converted into energy units (cm^{-1}) using Kayser's Tabellen der Schwingungszahlen(25), which include a correction from the wavelength in air to that in vacuum. Measurements of the patterns were found to be reproducible to about ± 2 microns on the plate, which corresponded to an uncertainty of about $\pm 0.004 \text{ cm}^{-1}$ in the pattern itself.

3.4 Determination of Magnetic Field Strength

To be able to measure accurate g-values from the observed Zeeman patterns of holmium, the magnetic field strength must be known to within the percentage error of measurement of the plates. This error was found to be ± 1 to 3 microns for the sharper lines, which corresponded to an uncertainty of about

± 0.002 to 0.006 cm^{-1} (at 5000\AA) in the line itself. Thus the percentage error of a measured splitting in a pattern averaged about 0.1%. The uncertainties in actual measurements were often much larger, though, due to the frequent broadening of lines in a Zeeman pattern as a result of the wide holmium hyperfine structure.

The lack of data on g-values for holmium energy levels necessitated the use of patterns of other elements for field strength determinations. The initial method employed here was to photograph the neon spectrum immediately following the photograph of holmium by replacing the holmium lamp with a neon lamp, without switching off the magnet between these exposures. By referring to an accurate listing of neon g-values (26) it was possible to determine the field for the neon lamp to within 0.1%. Over the period of an individual exposure the field itself had been checked and found to be stable to better than $\pm 0.1\%$. The greatest error was expected to result from unavoidable slight variations in the positioning of the holmium and neon lamps in the magnet cavity, since the field was known not to be strictly uniform over the entire gap.

In order to establish the reliability of the above field measurements, Zeeman patterns of impurity lines in the original holmium spectrum were sought. It was indeed fortunate that patterns for three ground state transitions of neutral europium appeared on the plates, two of these being completely resolved. One of the patterns is shown in figure 4 . The existence of an accurate g-value for the ground state of europium from atomic beam investigations (27) allowed accurate field calculations using these patterns. The ground state g-value for holmium was also available, but the observed Zeeman patterns for all three known ground transitions were heavily reversed and unresolved, making them useless for field calculations.

The resulting field values were more consistent over all six of the neon patterns than over the two europium patterns, but there was a significant difference in their averages. The neon field was about 0.4% higher than that for the europium, and hence for the holmium as well. This discrepancy is slightly greater than the 0.3% found during earlier experiments in this laboratory with gadolinium (28). Thus the neon method was not suitable here for field calibration since accurate holmium g-value results were desired.

The method nevertheless can be very convenient to use if a slight loss in accuracy is acceptable and better standards are unavailable.

The two Eu I patterns used here had been measured previously by Russell, Albertson, and Davis (29). Upon comparison with their published measurements an error was discovered in their listing of the σ components for $\lambda 4661$. Using their g-values the patterns should have been listed as:

4661: (0.139, 0.417, 0.700, ...) 1.282, 1.563, 1.844,
2.125, ...

4594: (0.106, 0.332, 0.554, 0.767, ...) 0.999, 1.217,
1.437, 1.656, ...

The atomic beam g-value for the ground state was then used with our patterns to calculate an average field value (27966 ± 20 gauss). This gave the following values for our patterns:

4661: (0.140₁, 0.421₄, 0.707₁, ...) 1.287₂, 1.575₄,
1.854₃, 2.132₁, 2.393₄, ...

4594: (0.109₁, 0.333₂, 0.545₆, ...) 0.987₂, 1.224₂
1.448₄, 1.668₂, 1.883₆, 2.114₂, 2.330₂, ...

Each subscript denotes the uncertainty in the last figure, derived from the standard deviation of several measurements of the splitting. The resulting g-values for the levels involved are:

$$\begin{array}{ll}
 4661: & g_{\frac{5}{2}} = 2.275_1 \\
 & g_{\frac{7}{2}} = 1.99337_7 \text{ (atomic beam).} \\
 4594: & g_{\frac{9}{2}} = 1.774_1
 \end{array}$$

The actual transitions are

$$\begin{array}{ll}
 4661: & 4f^7 6s 6p({}^8P_{\frac{5}{2}}) - 4f^8 6s^2 ({}^8S_{\frac{7}{2}}) \\
 4594: & 4f^7 6s 6p({}^8P_{\frac{9}{2}}) - 4f^8 6s^2 ({}^8S_{\frac{7}{2}}).
 \end{array}$$

CHAPTER IV

EXPERIMENTAL RESULTS

4.1 Introduction

The experimental portion of this project consisted of making efficient electrodeless lamps and utilizing them as light sources to obtain line spectra and Zeeman patterns for holmium. The lamps are discussed in detail in Chapter III. In the present chapter limited lists containing the best hyperfine and Zeeman patterns observed for Ho I are presented, with interpretations being attempted for many of these. The Zeeman results are, to the author's knowledge, the first ever published for holmium.

4.2 Hyperfine Structure Patterns

The line spectrum of holmium was photographed at high dispersion ($0.5\text{\AA}/\text{mm.}$ in the 10th order) over nearly all of the range $3600\text{--}9000\text{\AA.}$ From this, measurements were made of 25 lines displaying clear hyperfine structure and having at least four of the expected eight components resolved. The number of strong components in a hyperfine pattern results from an energy level

being split into either $(2J+1)$ or $(2I+1)$ hyperfine structure levels, whichever is the smaller. Here J is the total electron angular momentum quantum number of the level and I is the nuclear angular momentum quantum number (nuclear spin). The nuclear spin of holmium is $7/2$ so that unless J is less than $7/2$ exactly 8 levels will always be formed. Since nearly all terms in a complex structure such as that for holmium yield only high J -values, patterns with less than eight components will rarely occur.

Of the 25 lines measured, 11 were fully resolved, and these are listed in Table 2. For each pattern the first row contains the measured intervals between adjacent components, along with their total sum; the second row gives the decimal ratio of each interval to the widest; the third row lists earlier measurements by Belyanin (30) of these patterns (his results do not extend above 6500\AA).

It is immediately to be noticed that all 11 patterns are shaded to the red. Referring to Belyanin's data one finds that 30 out of the 37 Ho I lines listed are shaded to the red, as compared with only 19 out of 34 Ho II lines being shaded to the red. A second noticeable feature is that about half the patterns show large deviations from the interval rule, which usually is the result

Table 2

FULLY-RESOLVED HYPERFINE PATTERNS OBSERVED IN THE HO I SPECTRUM

Wavelength (Å)	Shading	Observations (10 ⁻³ cm ⁻¹)										Total	
		Intervals											
4641.70	r	254	225	200	175	158	132	97					1241
		1	.89	.79	.69	.62	.52	.38					
		270	225	210	175	150	150	100					
5674.70	r	218	204	191	180	169	140	130					1239
		1	.94	.88	.83	.78	.64	.59					
		215	200	195	180	160	145	140					
5948.03	r	172	147	149	129	126	120	85					928
		1	.86	.87	.75	.73	.70	.49					
		160	150	140	130	120	110	100					
5982.90	r	167	142	140	138	112	107	96					902
		1	.85	.84	.83	.67	.64	.58					
		160	150	140	135	125	110	90					
6133.60	r	203	194	183	175	162	146	142					1205
		1	.96	.90	.86	.80	.72	.70					
		210	190	180	175	150	160	135					
6156.58	r	210	212	195	183	184	155	138					1277
		1	1.01	.93	.87	.88	.74	.66					
		215	200	195	185	170	160	150					
6234.17	r	199	191	189	178	154	146	138					1195
		1	.96	.95	.89	.77	.73	.69					
		200	195	185	170	155	150	125					
6372.59	r	139	150	135	150	125	122	117					938
		1	1.08	.97	1.08	.90	.88	.84					
		145	150	140	135	130	120	100					
6550.97	r	188	173	173	158	151	133	116					1092
		1	.92	.92	.84	.80	.71	.62					
		133	123	119	113	107	92	80					
6680.46	r	1	.93	.90	.85	.81	.69	.60					767
		266	261	228	237	201	194	160					
		1	.98	.86	.89	.76	.73	.60					
6681.62	r	266	261	228	237	201	194	160					1547
		1	.98	.86	.89	.76	.73	.60					

of an additional interaction provided by the large quadrupole moment in the atom.

An attempt was made to relate the relative values of the intervals in each undistorted pattern to those expected theoretically. The interval rule states that the value of each interval is proportional to the F -value of the upper level, where F is the vector sum of I and J and varies from $I+J$ to $|I-J|$. This means the widest interval varies as $(I+J)$, the next as $(I+J-1)$, and so on. With the nuclear spin for holmium being known ($I=7/2$), the relative values of the measured intervals should be able to be matched to relative values for theoretical intervals based upon some J -value. This matching would thus yield the J -value of the level having the hyperfine structure (assuming that each wide pattern represents a transition between two levels of which only one has appreciable hyperfine structure).

In fact, only one of the patterns (4641\AA) was consistent enough to yield a likely J -value, this being $13/2$. The remaining patterns indicated J -values from about $21/2$ to $31/2$. It is somewhat surprising that such high J -values should appear for, if they are real, this means that they represent only the lowest levels of the lowest terms of excited configurations, and there is no reason

why transitions from only these levels should be seen.

Some of these possible terms in Ho I are

$$4f^{10} [^1(IKLN), ^3(HIKLM)] 5d6s6p$$

$$4f^{10} [^1(HIKLN), ^3(GHIKLM)] 5d^2 6s$$

$$4f^{11} [^2(KL), ^4I] 5d6s.$$

Each term has at least one level with J as high as 21/2 and each configuration contains an unpaired s-electron which tends to cause wide hyperfine structure.

4.3 Zeeman Patterns

The Zeeman spectrum of holmium was photographed over most of the range 4100-6800Å, using a field of 28 kilogauss. Of the 44 patterns chosen for measurement and interpretation, only eight were good enough to yield g-values. The observed patterns are listed in Table 3, with the separation of the most intense components underlined, the π -component separations shown in parentheses, and the uncertainty in the last digit for each separation indicated as a subscript. The calculated g-values appear in table 4.

The next two pages are devoted to brief descriptions and interpretations of the individual patterns.

- 1) 4105.6 Good, previously unassigned, $\Delta J=0$, $J=9/2$,
Ho I line, $\Delta g=0.277$, $g_1=0.862_2$, $g_2=1.139_2$
- 2) 4112.00 Poor, π 's shade-in, fair, σ 's poor,
 $\Delta J=0$, $J \geq 11/2$, $\Delta g=0.198$
- 3) 4112.72 Fair, π 's masked, σ 's good but overlapped
and blended, $\Delta J=0$, $J=5/2$, $\Delta g=0.575$,
 $g_1=0.565_2$, $g_2=1.140_2$, impurity line ?
- 4) 4116.73 Fair, π 's shade-out, σ 's shade-in, $\Delta J \neq 0$,
 $J \geq 7/2$, $\Delta g=0.185$
- 5) 4119.35 Unresolved, narrow, π 's shade-in ?, $\bar{g}=1.27$
- 6) 4142.19 Unresolved, narrow, $\bar{g}=1.18$
- 7) 4219.10 Good, σ 's shade-in, π 's shade-out, $\Delta J \neq 0$,
 $\Delta g=0.239$, $J_1=9/2$, $J_2=11/2$, $g_1=1.223_1$,
 $g_2=1.462_1$
- 8) 4223.47 Very good, σ 's shade-in, π 's shade-out, $\Delta J \neq 0$,
 $\Delta g=0.236$, $J_1=9/2$, $J_2=11/2$, $g_1=0.868_1$,
 $g_2=1.104_1$
- 9) 4264.05 Good, $\Delta J=0$, $J=15/2$, $\Delta g=0.186$, $g_1=1.012_2$,
 $g_2=1.198_2$
- 10) 4266.04 Fair, π 's shade-out, σ 's shade-out,
 σ 's overlapped and blended, $\Delta g=0.255$,
 $J_1=11/2$, $J_2=9/2$, $g_1=1.012_2$, $g_2=1.267_2$
- 11) 4497.7 Unresolved, narrow, $\bar{g}=1.26$
- 12) 4833.32 Poor, unresolved, $\bar{g}=1.18$
- 13) 4922.73 Unresolved, wide, $\Delta J=0$, $\bar{g}=1.19$
- 14) 4934.89 Complex, partially resolved, π 's shade-out,
 σ 's shade-out, $\Delta J \neq 0$, $\Delta g=0.25$
- 15) 5028.17 Unresolved, fairly sharp, $\bar{g}=1.11$
- 16) 5074.34 Unresolved, fairly sharp, $\bar{g}=1.18$
- 17) 5330.11 Fair, π 's shade-in, outer σ 's poor, $\Delta J=0$,
 $J=15/2$, $\Delta g=0.165$, $g_1=1.172_5$, $g_2=1.007_5$

- 18) 5381.40 Poor, σ 's unresolved and narrow, π 's one sharp pair, $\Delta J=0$, $\bar{g}=1.33$
- 19) 5384.97 Good, π 's shade-out, σ 's shade-in, $\Delta J \neq 0$, $J \geq 11/2$, $\Delta g=0.134$
- 20) 5445.39 Poor, unresolved, $\bar{g}=1.21$
- 21) 5504.51 Unresolved, narrow, $\bar{g}=1.16$
- 22) 5553.14 Unresolved, narrow, $\Delta J \neq 0$, $\bar{g}=1.18$?
- 23) 5573.96 Unresolved, sharp, $\bar{g}=1.20$
- 24) 5972.76 Poor, unresolved, wide, π 's split, $\Delta J=0$?, $\bar{g}=1.02$
- 25) 5973.52 Poor, unresolved, narrow, $\Delta J \neq 0$?, $\bar{g}=1.19$
- 26) 6002.04 Poor, $\Delta J=0$, $J=11/2$, $\Delta g=0.101$, σ 's unresolved and wide, $\bar{g}=(\sigma_{\max}+\sigma_{\min})/2=0.95$, $g_1=0.90$, $g_2=1.00$
- 27) 6060.31 Unresolved, sharp triplet, $g_1 \approx g_2=1.23$
- 28) 6191.68 Unresolved, sharp, $\bar{g}=0.79$
- 29) 6208.65 Unresolved, narrow, $\bar{g}=1.21$
- 30) 6745.05 Poor, σ 's unresolved, wide, $\Delta J=0$, $\bar{g}=1.13$

TABLE 3

ZEEMAN PATTERNS OBSERVED IN Ho I

Transition Wavelength (Å)	Pattern
1) 4105.6	$(\dots, 0.414_3, 0.692_1, 0.974_1, \underline{1.249}_2)$ $\dots, 0.707_1, \underline{0.986}_2, 1.270_3, 1.555_1, 1.830_2,$ 2.099_2
2) 4112.00	$(\dots, 0.281_4, 0.485_4, 0.691_4, 0.907_5, \underline{1.123}_4)$ $\dots, 1.382_3, 1.567_3, 1.787_7, 2.002_9, \dots$
3) 4112.72	$(\dots) -0.27_1, 0.27_1 [\text{blend}], \underline{0.853}_2, 1.432_2,$ 1.989_5
4) 4116.73	$(\dots) 1.339_2, 1.525_6, \underline{1.907}_2$
5) 4119.35	$(\dots) 1.267_1$
6) 4142.19	$(0.000) 1.178_6$
7) 4219.10	$(\underline{0.122}_2, 0.360_7, 0.595_1, 0.819_4, \dots)$ $1.084_4, 1.351_4, 1.587_2, 1.824_6, 2.060_2,$ $2.299_3, \underline{2.537}_1$
8) 4223.47	$(\underline{0.117}_1, 0.357_2, 0.590_1, 0.827_3, \dots)$ $1.221_4, 1.458_1, 1.694_1, 1.929_1, \underline{2.166}_1$

(continued)

Wavelength	Pattern
9) 4264.05	$(\dots, 0.269_4, 0.485_3, 0.648_6, 0.826_7, 1.013_2,$ $1.219_1, \underline{1.427}_1) \quad 1.646_4, 1.842_6, 2.043_9,$ $\underline{2.221}_4, 2.419_2$
10) 4266.04	$(\underline{0.123}_2, 0.386_1, 0.636_5, 0.896_7, 1.169_6)$ $-\underline{0.14}_1, 0.14_1 [\text{blend}], 0.39_1, 0.637_1, 0.896_6,$ $1.143_1, 1.394_5, 1.640_2, 1.897_4, 2.152_7$
11) 4497.7	(0.000) 1.256_5
12) 4833.32	(0.176 ₉) 1.181_9
13) 4922.73	(0.232 ₉) 1.194_9
14) 4934.89	(<u>0.123</u> ₂ , 0.374 ₂ , ...)
15) 5028.17	(0.000?) 1.107_4
16) 5074.34	(0.000) 1.179_2
17) 5330.11	$(\dots, 0.587_1, 0.742_4, 0.904_3, 1.070_1, 1.225_3)$ $\dots, \underline{1.421}_1, 1.582_1, 1.742_7, 1.903_4, 2.093_3,$ 2.267_3
18) 5381.40	(0.059 ₂) 1.325_3
19) 5384.97	$(\underline{0.068}_1, 0.205_2, 0.332_1, 0.466_3, \dots)$ $\dots, 1.800_1, 1.933_1, \underline{2.073}_2$

(continued)

Wavelength		Pattern	
20)	5445.39	(0.122 ₉)	1.214 ₉
21)	5504.51	(0.000)	1.155 ₉
22)	5553.14	(0.000)	1.181 ₉
23)	5573.96	(0.000)	1.203 ₃
24)	5972.76	(0.165 ₉)	1.024 ₂
25)	5973.52	(0.000)	1.188 ₂
26)	6002.04	(... , 0.152 ₂ , 0.259 ₂ , 0.351 ₃ , 0.452 ₁ , <u>0.546₁</u>) 0.399 ₆ ----- 1.497 ₂	
27)	6060.31	(0.000)	1.227 ₂
28)	6191.68	(0.000)	0.790 ₁
29)	6208.65	(0.000)	1.211 ₉
30)	6745.05	(0.232 ₉)	1.132 ₄

TABLE 4

CALCULATED G-VALUES FOR HO I

Transition Wavelength (Å)	J_1	g_1	J_2	g_2
4105.6	9/2	0.862 ₂	9/2	1.139 ₂
4112.72	5/2	0.565 ₂	5/2	1.140 ₂
4219.10	9/2	1.223 ₁	11/2	1.462 ₁
4223.47	9/2	0.868 ₁	11/2	1.104 ₁
4264.05	15/2	1.102 ₂	15/2	1.198 ₂
4266.04	11/2	1.012 ₂	9/2	1.267 ₂
5330.11	15/2	1.172 ₅	15/2	1.007 ₅
6002.04	11/2	0.90 ₁	11/2	1.00 ₁

CHAPTER V

COMPUTER TECHNIQUES APPLIED
TO THE ANALYSIS OF COMPLEX SPECTRA5.1 Introduction

The enormous task which one faces in analyses of complex spectra, both in the sorting of experimental data and in the performing of lengthy and tedious theoretical calculations, demands the use of digital computers to achieve any sense of completeness within a reasonable length of time.

Before the arrival of the computer, such analyses were carried out by hand with, at best, the assistance of a mechanical calculating machine. Initial sorting of experimental data was usually based upon application of the combination principle, to which every spectrum must of course conform, though not necessarily in an obvious way. An early advancement in the procedure for seeking these important wave number separations was Harrison's simple but ingenious mechanical interval sorter (31). The limit in "resolution" to which this machine could produce detectable sets of differences was about $\pm 0.02 \text{ cm}^{-1}$,

certainly no restriction on usual accuracy with the combination principle. Today, of course, the same interval sorting procedure is handled by computers, which have the advantage of being able to do more than just identify sets of equal differences. Fitting of proposed experimental or theoretical levels into a known level scheme, calculating unknown allowed transitions to suggest new wavelengths of lines, and simplifying the analysis of complex Zeeman patterns (especially those with wide hyperfine structure) all are examples of computers being applied to investigations of atomic structure.

The method of seeking constant sums and/or differences is, as mentioned, the basic starting point for the analysis of any unknown spectrum. However, when attacking the extremely complex spectra of the rare earth elements, with many thousands of lines per spectrum, the number of chance occurrences of any particular difference (which varies as the square of the number of lines considered) begins to destroy the value of the combination principle alone. Here the reduction of experimental hyperfine structure and Zeeman Effect data and above all the incorporation of accurate theoretical energy structure

predictions into the analysis become necessary. The volume alone of the numbers and parameters in such procedures necessitates the use of computers.

5.2 Discussion of Programs

The present project was partly concerned with seeking energy levels for neutral holmium beyond the three known levels. Therefore, computer programs were written to perform the following:

- (a) convert wavelengths in air to wavenumbers in vacuum, using an iterative process with Edlén's dispersion formula (32);
- (b) calculate all possible differences between pairs of an input list of wavenumbers, compare all differences to one another, and print out sets having at least a specified number of differences that are equal within a specified accuracy, along with the two wavenumbers which formed each difference;
- (c) calculate all possible differences between pairs of an input list of wavenumbers and print the entire list of differences with pairs of wavenumbers in numerical order, giving the numerical difference between

- each adjacent wavenumber difference as well;
- (d) attempt to fit postulated new levels to combinations of known levels and known transitions;
 - (e) calculate all possible differences between pairs of input wavenumbers and print out those which fall within a specified range or ranges of values.

Detailed descriptions of these programs appear in the appendix.

Program (a) was used to avoid the tedious procedure of looking up each wavelength individually in the wavenumber tables. The results agreed fairly well with the published values. A spot check over the entire wavelength range considered (2000-9000 \AA) yielded a maximum variation of 0.009 cm^{-1} from the published values, with most calculated values being within 0.005 cm^{-1} or less of their published values. These slight discrepancies could not be overcome, even through the use of double precision numbers on the computer and continuing the iteration until successive results differed by less than 0.0001 cm^{-1} . Since the initial wavelengths used were only quoted to the nearest 0.01\AA , which represents from 0.25 cm^{-1}

at 2000\AA down to 0.011 cm^{-1} at 9000\AA , these variations do not have a significant effect upon the wavenumber values.

To test the remaining programs, they were applied to a set of lines of neutral thulium obtained from the National Bureau of Standards tables. The success of the programs was evident with the obtaining of all the known pairs of lines which form the ground state doublet ($0, 8771\text{ cm}^{-1}$), along with numerous additional significant differences enabling the immediate fitting of some 40 lines to the levels listed by Blaise and Camus (33).

5.3 Application to Holmium

(a) Neutral Holmium (Ho I)

The line list consisted of the 333 lines assigned to the first spectrum of holmium in the National Bureau of Standards intensity tables. The computer used for all computations was an IBM 360, having 64,000 word capacity. Due to the enormous amount of data generated by the programs, only a limited line list could be submitted at one time to avoid exceeding the computer memory capacity. The maximum number of lines capable of being handled at once varied from 180 to 200, depending upon which program was being used.

Initially, sets of wavenumber pairs having the same difference were sought from 200 lines. Several attempts were made for various tolerances, but no intervals of any apparent significance were revealed for Ho I. Next a more careful selection was made of 100 lines, including all strong NBS lines, all 64 lines assigned to Ho I in King's temperature classification (34), and all lines observed in the absorption spectrum of holmium (35). Since this compilation was assumed to represent the heart of the spectrum, out of which most low level structure would very likely arise, all possible differences between these wavenumbers were printed out in consecutive order.

In particular, it was thought that the intervals in the ground multiplet $4f^{11}6s^2(^4I)$ may be distinguishable using this listing. This was quite a reasonable supposition since the most prominent transitions in the rare earths are f^n6s6p to f^n6s^2 transitions, and the expected height of the f^n6s6p configuration (above about $15,000\text{ cm}^{-1}$) generally coincided with the magnitudes of the strongest listed transitions (about $24,000\text{ cm}^{-1}$). Unfortunately, the desired outstanding sets of equal wavenumber differences did not appear. This result was entirely unexpected, for more fully analyzed spectra of other lanthanides were known to show both King's lines and absorption lines predominantly involving lower levels within only a few thousand wavenumbers of the ground level. The list was then more carefully combed in an attempt to extend the Ho I level structure using possible significant intervals involving one or more of the three classified ground state transitions. These could not be arranged in any self-consistent level system for either the lowest interval with the ground state or the upper intervals between their originating levels.

At this point it was suspected that more lines needed to be considered before the real intervals could be found. Since the computer could not handle any more

lines at one time, it was decided that a complete listing of all possible wavenumber differences up to 6000 cm^{-1} between all pairs of the 333 lines would be useful for reference, and this was compiled part by part, using different portions of the wavenumber list for each input, but overlapping sufficiently to include all possible combinations up to 6000 cm^{-1} . This library of differences was then used to check the significance of any proposed interval up to 6000 cm^{-1} . It immediately confirmed the author's suspicions (supported by private communication from Spector) about the validity of the ^4I levels claimed by Belyanin (9), for his intervals did not appear with any significance at all. Then a search was made in the vicinity of the fairly accurately calculated intervals of Conway and Wybourne (8) for the ^4I ground term, also without success. A few groups of two or three close differences could nearly always be found, but attempts to link pairs of transitions between adjacent ground intervals by the transition to their common level always failed. This does not rule out their validity, but without any such self-consistency the intervals must be viewed as doubtful.

The final attempt at discovering the ground multiplet levels utilized the experimentally determined levels for

Ho III (6). For all neutral lanthanides having the $f^n s^2$ ground configuration (as for holmium), the ground configuration of the doubly-ionized spectrum is f^n . It turns out that the $6s^2$ shell has very little effect upon the f^n configuration, and thus the ground multiplets for the first and third spectra are nearly identically spaced. For praseodymium the maximum level shift is 1.5%, for samarium 0.2%, and for thulium 0.03%, the levels of the neutral atom being the lower in all cases. Thus the ground term levels for Ho I are likely less than 1% lower in value than the known Ho III levels of 5438, 8644, 10770 cm^{-1} . This would agree magnificently for the first level with the previously mentioned calculation of Conway and Wybourne (5428 cm^{-1}) or with a recently proposed value of 5426.4 cm^{-1} by Spector (36). The other two theoretical levels of Conway and Wybourne (8722, 10980 cm^{-1}) are also in fairly close agreement, though somewhat too high. In spite of all this agreement the intervals do not appear significantly among the list of differences.

So it appears that even the NBS list of lines is insufficient to start the analysis, and it should be realized that 333 lines is actually very few for a complex lanthanide spectrum. The wavelength list must be extended,

particularly into the infrared, and wavelength identifications must be made very accurately to reduce the required tolerances and hence the number of random coincidences in the analysis. The importance of the infrared region is its smaller wavenumber error for a given wavelength measurement error and the fact that infrared transitions directly connect many of the low-lying, often overlapping configurations.

The near infrared spectrum of holmium (up to 9000\AA) was photographed during this project, with the hope of eventually obtaining Zeeman patterns as well. The combination of low intensity in the infrared along with the required slower photographic emulsion necessitated extremely long exposure times (about one hour at high lamp intensity gave little more than the NBS lines).

(b) Singly-Ionized Holmium (Ho II)

The NBS line list for Ho II totals 547 lines. Though Ho II was not considered as completely as was Ho I, the results appear a bit more encouraging. The analysis was based entirely upon the four classified lines that specify the lowest interval and an upper interval, as published by Sugar (37). First, the entire wavenumber list was scanned to pick out all differences

close to Sugar's lower interval of 637.8 cm^{-1} . These differences are listed in table 5. Each real pair of transitions to the ground interval specifies an upper energy level. For the initial analysis the 16 most likely real pairs were chosen and all differences between their upper energy levels were calculated. Then these intervals were checked for significance by comparison, using the computer, to a list of all differences between pairs of wavenumbers from a chosen portion of the Ho II spectrum.

Independently, using these same wavenumbers, a listing was computed for all differences that lay in the region near the next expected level in the ground term, about 1185 cm^{-1} , given by the interval rule for LS coupling, which is normally a reasonable assumption to apply to the lowest levels of the lanthanides. From this list those differences that were repeated several times within reasonably small tolerances were isolated and compared with the previous results for the upper level intervals. The outcome was the eventual construction of the level scheme shown in figure 6.

This level system is essentially three independent schemes, related only by their connection to the lowest interval, 637.8 cm^{-1} , with the level 27574.8 cm^{-1} being common to the left and right schemes as well. There are

TABLE 5

POSSIBLE PAIRS OF TRANSITIONS FORMING THE 637.8 cm^{-1}
INTERVAL IN SINGLY-IONIZED HOLMIUM

<u>DIFFERENCE</u>	<u>NBS</u> <u>INTENSITY</u>	<u>KING</u>	<u>TRANSITIONS</u>	<u>WAVELENGTHS</u>
(cm^{-1})			(cm^{-1})	(Å)
637.54	18		26937.00	3711
	32		26299.46	3801
.66	36		29823.47	3352
	220		29185.81	3425
.68	22		29325.19	3409
	700		28687.51	3484
.68	12		27639.87	3616
	55		27002.19	3702
.69	18		28467.61	3511
	70		27829.92	3592
.70	18		29472.24	3392.05
	40		28834.54	3467
.72	80	V	25914.70	3857
	10	III	25276.98	3955.05
.74	160		29275.04	3414.90
	32		28637.30	3490
.76*	1000		26234.24	3810
	140	IV	28596.48	3905
.76*	600	IV	24712.21	4045
	110	IV	24074.45	4152
.79	110		29899.47	3343
	600		29261.67	3416
.83	22		30884.84	3236
	22		30247.01	3305
.83	34	III	22326.94	4477
	13	V	21689.11	4609.32
.84	19		27574.84	3625
	18		26937.00	3711
.85	6		20128.37	4966
	6		19490.52	5129

(continued)

.88	3		33827.97	2955
	5		33190.09	3012
.92	1000		26330.84	3796
	1500	IV	25692.92	3891
.94	26		27082.87	3691
	32		26444.93	3780.37
.94	44	IV	23636.69	4229
	11		22998.75	4346
.94	6	V	21864.14	4572
	14		21226.20	4709
.94	19		35559.50	2811
	13		34921.56	2862
.95	44		29941.73	3338
	32		29303.78	3411
637.97	5		38933.23	2567
	7		38295.26	2610
638.02	26		34139.52	2928
	7		33501.50	2984
638.03	120	V	26008.14	3843
	36	V	25370.11	3940
.06	4		36729.92	2721
	24		36091.86	2769
.07	42		32784.02	3049
	22		32145.95	3109
.09	8		34803.39	2872
	14		34165.30	2926.09

*Classified by J. Sugar (37).

Ionization
Potential: 11.8 eV
(95,200 cm⁻¹)

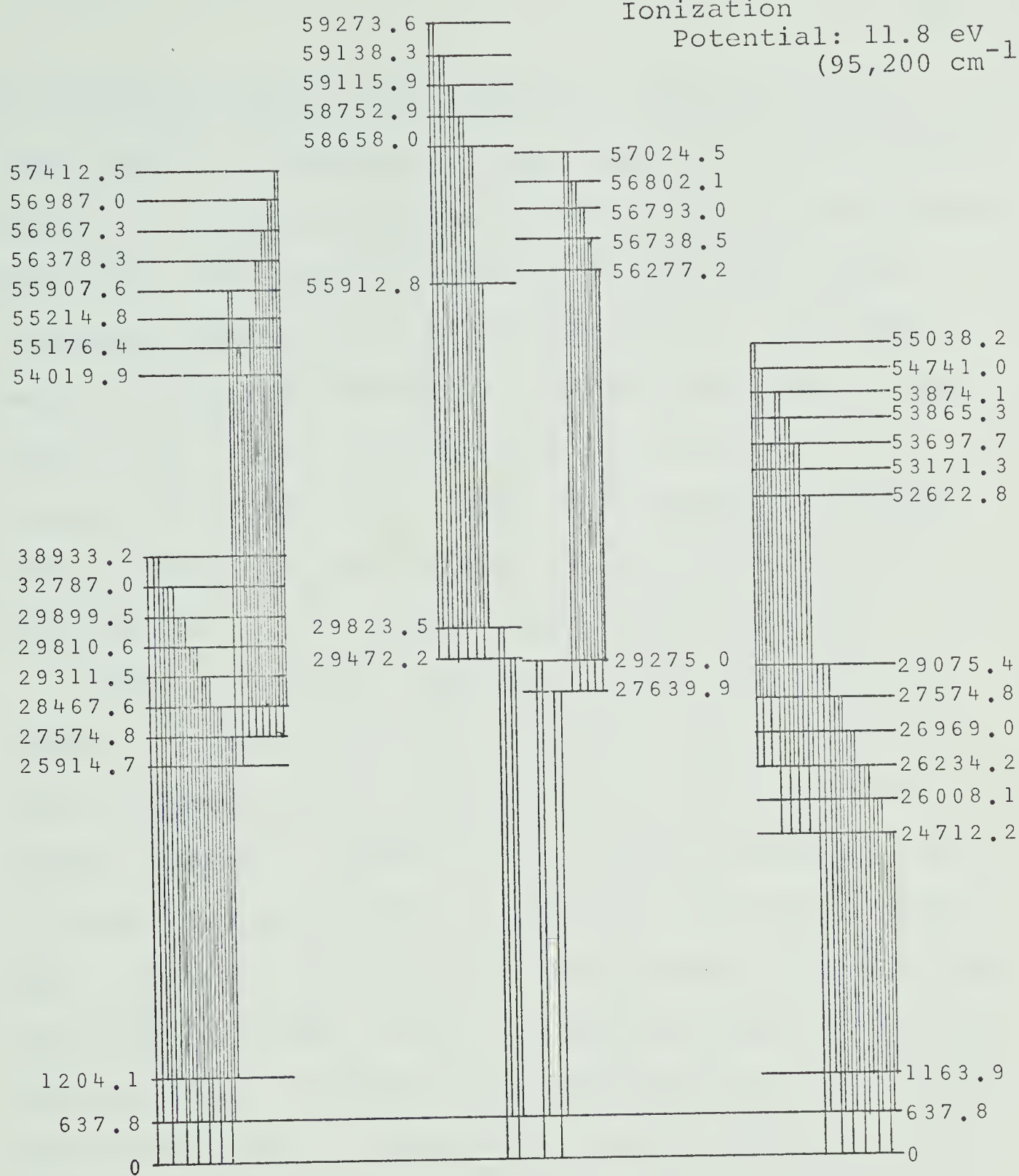


Figure 12

POSSIBLE LEVEL SYSTEM FOR SINGLY-IONIZED HOLMIUM

(not drawn to scale)

two possibilities for the $J=6$ level, 1163.9 cm^{-1} and 1204.1 cm^{-1} ; here the ground level has $J=8$, the 637.8 cm^{-1} level, $J=7$. To investigate the possibility of both levels being real, the position expected for the next term of the ground configuration was investigated. For other second lanthanide spectra the position was found to vary from 440 cm^{-1} (Er II) to 8957 cm^{-1} (Tm II), with the average about 1500 cm^{-1} . Thus it is certainly possible that one level is the 5I_6 level of the ground term and the other is the 3I_7 lowest level of the next term.

There are several weaknesses to the proposed level system. First is the wide tolerances allowed for some level fitting. This renders several of the classifications suspect. (Refer to the list of classified lines in the Appendix, page 97). Second is the lack of common upper levels in the left and right systems. All J -values are nearly the same, so the two systems should be strongly interconnected. Third is the unreliability of all levels above $50,000 \text{ cm}^{-1}$. These were included mainly to illustrate the significance of certain central intervals in the $20,000\text{--}30,000 \text{ cm}^{-1}$ region. Any level determined by only two transitions is spurious until confirmed. It should be recalled, however, that aside from determining the 637.8 interval, only a 200 line section of the Ho II

spectrum was considered. There are sure to be many further classifications fitting this system among the remaining lines. In spite of the weaknesses in many upper levels, the 1163.9 and 1204.1 levels appear to be real. The proposed structure should be made the object of further investigation.

CHAPTER VI

SUMMARY

Various techniques for analyzing complex spectra have been described and several of them applied to the first and second spectra of the rare earth metal holmium. The Zeeman effect for holmium has been photographed and initial results are given for Ho I. Several hyperfine patterns have also been measured. A computer analysis has yielded a possible level system for Ho II based upon the NBS line list and four previously-classified transitions. Finally, a bibliography updating the NBS bibliography for spectroscopic investigations of the lanthanide elements has been presented, along with a summary of the present states of analysis of the first and second lanthanide spectra.

The Zeeman results have illustrated the complexity involved when wide hyperfine structure is present in the energy levels. The resulting limited amount of interpretation possible for the patterns using normal techniques points out the need for a detailed consideration of the hyperfine structure and Zeeman effect together if sufficient data for an extensive term analysis of holmium is to be obtained.

The level analyses by computer methods have indicated that improvement of wavelength accuracy and extension into the infrared region are needed before the level structures of Ho I and II can be well understood. Possible level structures have been proposed for Ho II and require further confirmation. The Ho I level system has defied all attempts at discovering it. It would appear that the understanding of the level structures of both Ho I and II will rely heavily upon interpretation of an extended and improved wavelength list, with some assistance and confirmation from hyperfine and Zeeman patterns.



APPENDIX

PRESENT STATES OF ANALYSES OF THE FIRST AND SECOND LANTHANIDE SPECTRA

Element	Wavelength Range Recorded	Lines Observed	Lines Classified	Zeeman Patterns	Levels	Experimental Work in Progress
Ce I	2000-19000	26000	18000	>100	1115	N,H,L
Ce II	2500-19000		3600	427	316	N,H
Pr I	1741-5839	3532	x	x	4	N,O
Pr II	2400-8000	>2700	312	141	74	N
Nd I	2400-25000	26000	555	110	695	A,O
Nd II	2000-25000	5000	367	250	680	A,O
Pm I	2337-6872	>2200	714	xx	221	N,LRL
Pm II				x	200	N,LRL
Sm I	3350-25000	>2000	859	7	447	O
Sm II	3000-25000		1200	>300	325	O
Eu I	2428-9326	2200	1156	x	262	Ox,Ha
Eu II	2109-10165	2000	467	459	156	
Gd I	2734-10629	20000	1217	199	545	A,S
Gd II	2140-9000		1177	120	305	A,S
Tb I	3290-11650	24000	4810	600	354	A
Tb II	2400-7000	5000	138		135	A
Dy I	2300-9200	22000	x	x	315	O,LRL
Dy II			>100	x	250	O,LRL
Ho I	2500-8916	900	3	>200	3	N,S,E
Ho II			4		3	N,S,E
Er I	2100-12000	25000	>500	87	315	S,OR
Er II			>500	132	102	S,OR
Tm I	2513-25000	>900	>100	63	110	N,O,Ha
Tm II	2182-25000		>200	150	110	N,O

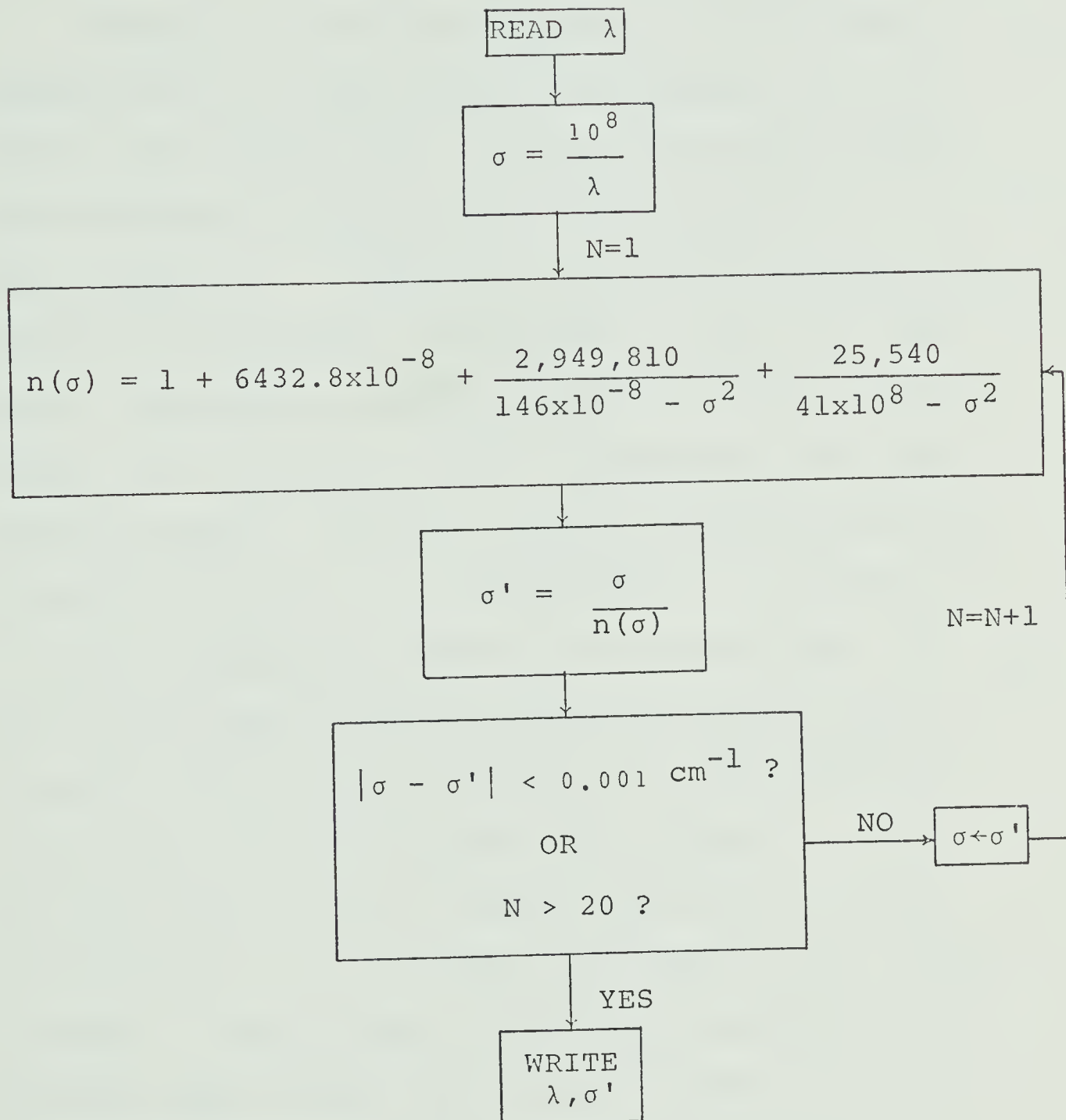
(continued)

Element	Wavelength Range Recorded	Lines Observed	Lines Classified	Zeeman Patterns	Levels	Experimental Work in Progress
Yb I	2000-12000	1800	>100	>200	80	N
Yb II		5100	4000	1000	315	
Lu I	2464-10730	253	124	40	51	L
Lu II	2195-8459	370	191	6	23	L

N--National Bureau of Standards
 H--Hebrew University
 A--Amsterdam
 O--Orsay, France
 LRL-Lawrence Radiation Laboratory, Berkeley
 S--Soreq, Yavne, Israel
 E--Edmonton
 OR--Oak Ridge
 L--London
 Ha--Hannover
 Ox--Oxford

x--Unpublished
 xx--Data unavailable
 to author

(a)

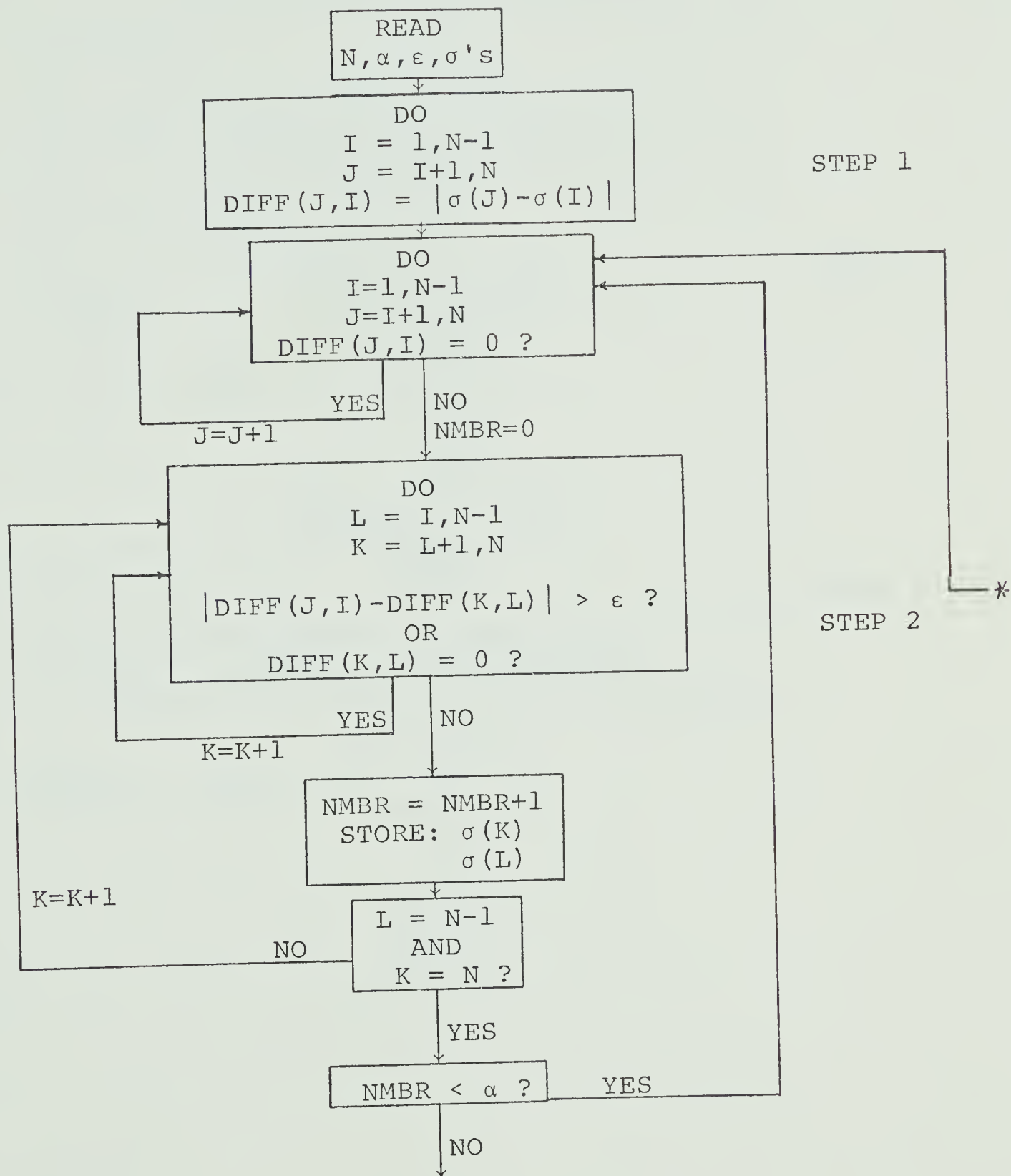


(b)

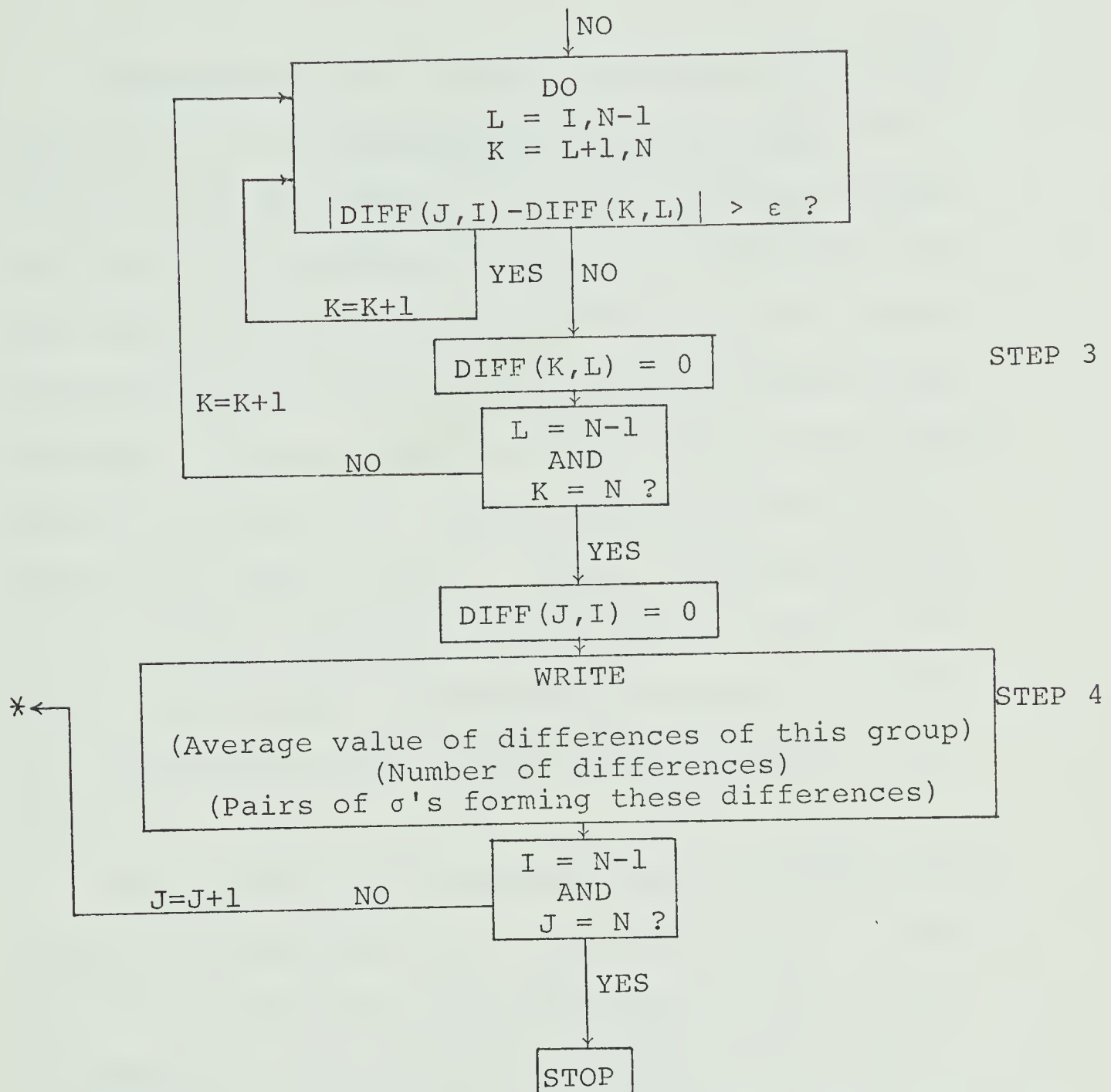
(Refer to flow diagram)

(Step 1). Calculate all possible differences between pairs of input list of wavenumbers and store them in the matrix DIFF (the two subscripts locating each difference in the matrix identify the two σ 's that formed it). (Step 2). Compare all elements of DIFF (i.e. wavenumber differences) to the (2,1) element. Each time an equal (within $\pm\epsilon$) difference is found, its originating pair of wavenumbers are temporarily stored. When all elements of DIFF have been checked, the set of equal differences is retained if it has a significant number (α) of equalities. If this is so, each equal difference is erased (Step 3) from the matrix DIFF (by setting its place equal to zero), and the data is printed out (Step 4). If the set does not have a significant number of equal differences, it is discarded with steps 3 and 4 being skipped. After either one of these procedures, the process begins again with the next element (3,1) of DIFF being compared to all subsequent elements.

(b)



(continued)

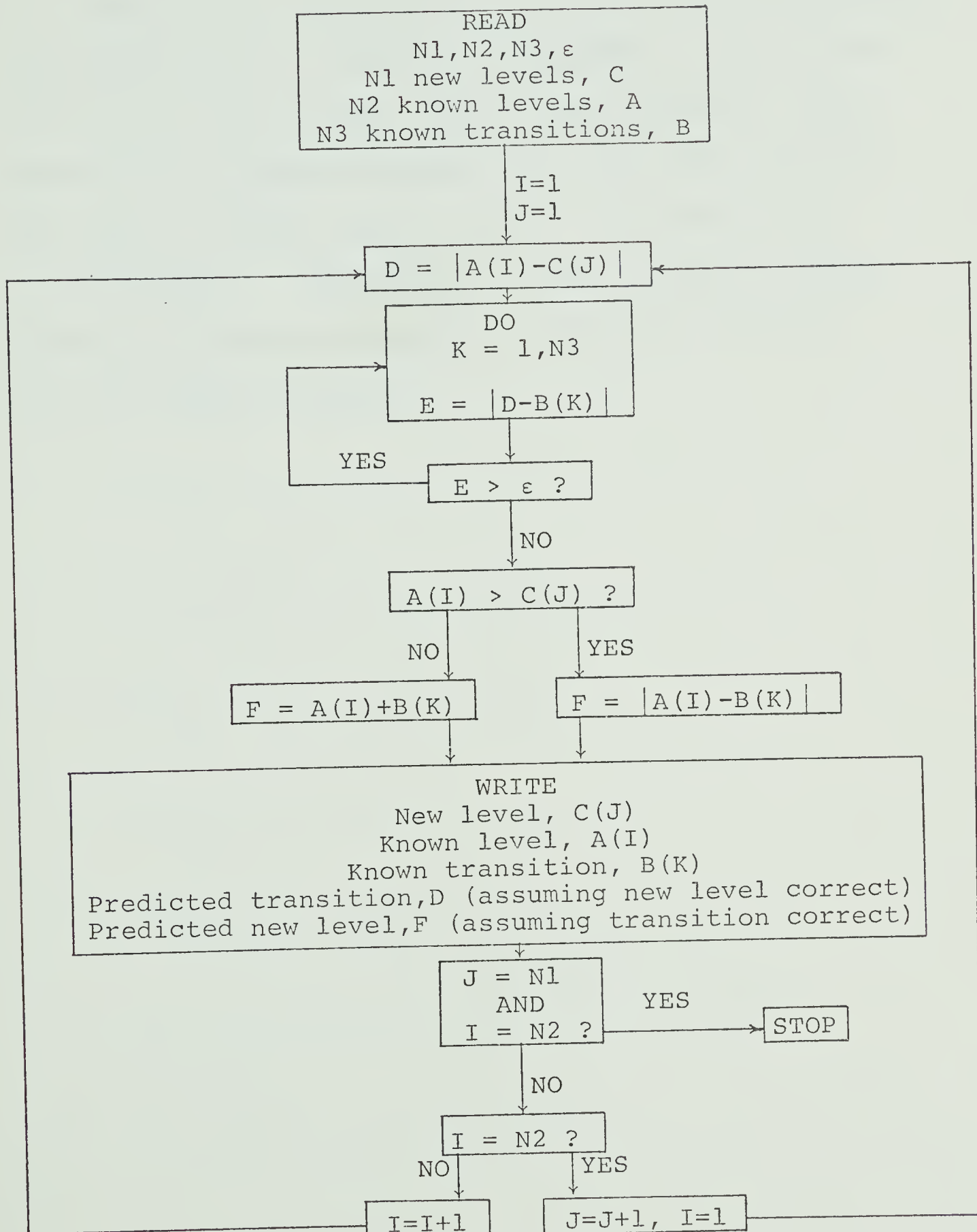


(c)

The matrix DIFF is again constructed from input list of N σ 's (in descending numerical order) and appears with the elements of each individual column ($J=I+1,N$) in ascending numerical order from the top. This means that the maximum DIFF (J,I) value always appears as one of the bottom elements of one of the columns. This particular maximum value of the entire matrix is sought for, stored, and its place in the matrix set equal to zero. Thus a continuous search of the bottom non-zero elements of the columns will yield, one by one, the desired consecutive listing (in descending order) of all the differences in the matrix.

Each DIFF (J,I) is printed as it is found, along with its originating $\sigma(J)$, $\sigma(I)$ wavenumbers. Also, the value separating each difference in this final consecutive listing from the preceding (i.e. next higher) one is printed beside the former, thus indicating at a glance when a series of differences are equal or nearly equal (which is the primary goal of the program).

(d)



(e)

After again constructing the matrix DIFF containing all differences of the input wavenumbers, each difference which falls between any of the M pairs of limits specified is picked out and listed under the appropriate pair of limits, along with its originating pair of wavenumbers. Then each of these groups of differences is sorted and printed in consecutive order as well for easier analysis.

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TRANSITIONS TENTATIVELY CLASSIFIED FOR Ho II
(see level diagram on p. 74)

Average Difference	Levels Forming Difference	Transitions Having This Difference	Actual Difference	Common Level
3984.7	29899.5, 25914.7	29899.46, 25914.70 29992.93, 26008.14 29261.67, 25276.98	3984.76 .79 .69	0 55907.6 637.8
892.8	28467.6, 27574.8	28467.61, 27574.84 28803.89, 27910.72 29412.15, 28519.01 27829.92, 26937.00 29837.80, 28944.90 29292.45, 28399.68 27639.87, 26747.17 26444.93, 25552.26	892.77 893.17 .14 892.92 .90 .77 .70 .67	0 56378.3 56987.0 637.8 57412.5 56867.3 55214.8 54019.9
1340.5	27574.8, 26234.2	27574.84, 26234.24 26937.00, 25596.48 28803.89, 27463.41 28506.65, 27166.18 27639.87, 26299.46	1340.60 .52 .48 .47 .41	0 637.8 55038.2 54741.0 53874.1
1522.1	26234.2, 24712.2	26234.24, 24712.21 29162.06, 27639.87 27910.72, 26388.59 28985.52, 27463.41 29153.13, 27631.09 25596.48, 24074.45	1522.03 .19 .13 .11 .04 .03	0 53874.1 52622.8 53697.7 53865.3 637.8
1635.1	29275.0, 27639.9	29275.04, 27639.87 29098.57, 27463.41 29153.13, 27517.99 28637.30, 27002.19 29384.48, 27749.43 29162.06, 27527.01	1635.17 .16 .14 .11 .05 .05	0 56738.5 56793.0 637.8 57024.5 56802.1

(continued)

351.2	29823.5, 29472.2	29823.47, 29472.24	351.23	0	59273.6
		29801.43, 29450.10	.33		55912.8
		26440.59, 26089.31	.28		637.8
		29185.81, 28834.54	.27		59115.9
		29643.69, 29292.45	.24		58752.9
		29280.61, 28929.41	.20		59138.3
		29666.04, 29314.87	.17		28467.6
1204.1	1204.1, 0	28467.61, 27262.11	1205.50*		29810.6
		29810.58, 28606.08	1204.50		32784.0
		32784.02, 31579.55	.47		29311.5
		29311.52, 28107.29	.23		29899.5
		29899.46, 28695.33	.13		27574.8
		27574.84, 26370.77	.07		38933.2
		38933.23, 37729.17	.06		29075.4
1163.9	1163.9, 0	29075.38, 27910.72	1164.66*		24712.2
		24712.21, 23548.28	1163.93		26008.1
		26008.14, 24844.24	.90		27574.8
		27574.84, 26410.97	.87		26969.0
		26969.04, 25805.20	.84		26234.2
		26234.24, 25070.52**	.62		

* Classification is doubtful

** Transition identified by Gatterer and Junkes (5)

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